A MONOGRAPH OF
VISCOMETRY

BY

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TO

D<small>R</small>. G. F. C. S E A R L E
WHO FIRST SHOWED ME
THAT PHYSICS MIGHT BE
AS INTERESTING AS
CHEMISTRY

PREFACE

IN spite of the extent of the literature dealing with viscosity that has appeared in scientific and technical periodicals, there have been singularly few text-books devoted to this important subject. Brillouin's *Leçons sur la viscosité des liquides et des gaz* (Gauthiers-Villars, Paris, 1907) may be regarded as classical in view not only of the excellent review which he gives of earlier work, but of the completeness of his mathematical treatment. In English there were available until recently only Dunstan and Thole's short monograph, *The Viscosity of Liquids* (Longmans, Green & Co., London, 1914) and Bingham's *Fluidity and Plasticity* (McGraw Hill Book Co. Inc., New York, 1922). During the preparation of the present monograph there has also appeared Hatschek's interesting and concise exposition, *The Viscosity of Liquids* (G. Bell & Sons, London, 1928).

Each of these books is chiefly concerned with the theoretical aspects of viscosity, such as its *raison d'être* and its relation to physical conditions and molecular structure. The methods of measurement have, therefore, been somewhat briefly discussed, except for a fairly full treatment by Bingham of the variable-pressure capillary-tube method. I have felt that there was need of a book devoted entirely to viscometry, in which an investigator should be able to find some account of most of the schemes which have been applied and some indication of the theoretical and practical difficulties that affect each of them. This monograph is an attempt to satisfy the need. It does not profess to be exhaustive or even to give complete references to the literature. There is a bibliography of eighty-two pages attached to Bingham's book, which will prove invaluable to any one who wishes to make a deeper study, as it has to me. I have intentionally avoided the inclusion of a section dealing with the viscosity of solids: the subject is too involved for summary treatment, and most of the methods of measurement are unlike those available for liquids or gases. I have thought it essential, however, to devote a chapter to the examination of 'plastic' or anomalous liquid systems; the reader may be referred to Hatschek's book for a fuller discussion of the theoretical importance of variable apparent viscosity in colloidal systems.

The frequency of the abbreviated citations Brillouin, *Leçons*,

and Bingham, *Fluidity and Plasticity*, in the numerical list of references appended to each chapter will serve to indicate, somewhat inadequately, the extent to which I have made use of the two books mentioned. I must also acknowledge the help which I have received from Mr. Winslow H. Herschel, of the Bureau of Standards: not only have we corresponded on the subject of viscometry for several years, but he has given me direct assistance by placing at my disposal unpublished manuscript which has facilitated the writing of Chapters IV and IX. I wish to record my gratitude to Dr. Hilding Faxén, of Uppsala, for reading my discussion of the 'falling-sphere method' and giving me a number of criticisms on the first half of Chapter VIII. I have also to thank Mr. W. F. Higgins, of the National Physical Laboratory, for comments on the section dealing with Redwood viscometers.

Illustrations of viscometers have been freely culled from the literature; my thanks are tendered and formal acknowledgement is here made to the firms, authors, and learned societies mentioned in the text, for permission to reproduce them. I crave indulgence from any of whom I may have failed to make due mention or from whom I may inadvertently have omitted to obtain permission. I am particularly indebted to all who have assisted by the loan of blocks or by the supply of electros.

Finally, my thanks are due to the Department of Scientific and Industrial Research and to the Director of the National Physical Laboratory for permission to publish this monograph.

<div align="right">GUY BARR.</div>

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INTRODUCTORY AND HISTORICAL NOTES

1. Qualitative tests for viscosity. The craftsman distinguishes between liquids which are thin or thick, light or heavy, without necessarily implying any comparison of opacity or density, and grades them in order of thickness or heaviness by one or more of four tests: (*a*) he may rock the container and see or feel how large a surge of liquid is produced or how rapidly the wave dies down; (*b*) he may note the resistance offered to the motion of a stirrer; (*c*) he may observe the form of the falling column which results when he pours the liquid over an edge or allows it to drain from a rod; (*d*) he may place a quantity of the liquid on a smooth surface and notice how it 'runs'. A scientific but unpractised onlooker will recognize gross differences of behaviour in such tests, but the finer distinctions, on which the success of the ensuing operation may depend, demand long familiarity with the particular class of material examined. In view of the large scale on which certain liquid products are now manufactured or compounded and of the frequent introduction of new ingredients for the use of which experience is lacking, it becomes necessary to be able to obtain in the laboratory some accurate indications of those properties which have hitherto been estimated by skilled workers.

This monograph contains some account of most of the methods which have been developed for the measurement of viscosity, the characteristic on which chiefly depends the behaviour of a liquid in any of the crude tests above enumerated. It happens that each of these qualitative tests involves another property, surface tension or density, in such a manner that it has not been found convenient to elaborate the experiment into a precise method of viscometry; see, however, Watson[1] and Trouton,[2] who showed respectively that observation of the damping of waves of a mobile liquid and measurement of the shape of a pendant column of pitch might be made the basis of an estimation of viscosity. Before any absolute method could be worked out it was necessary that some hypothesis should be formulated as to the mechanism of the phenomena.

2. Newton's hypothesis. Such an hypothesis was first put forward by Newton in his *Principia*. The second Book, devoted

to an analytical and experimental study of the resistance offered
to the motion of solids through fluids, contains equations for the
period and decrement of the oscillations of a pendulum calculated
on the assumptions that the resistance is proportional (i) to the
velocity, (ii) to the square of the velocity, or (iii) to a function
involving both the velocity and its square. Section I which deals
with assumption (i) concludes with the *Scholium*: 'Caeterum
resistentiam corporum esse in ratione velocitatis, Hypothesis est
magis Mathematica quam Naturalis. Obtinet haec ratio quam-
proxime ubi corpora in Mediis rigore aliquo praeditis tardissime
moventur . . .' After an account of his experiments on various
pendulums oscillating in air, in water, and in mercury, which
agreed with assumption (iii), he concluded (*Scholium generale* fol-
lowing section VI): '. . . sed omnia experiri non vacat, et ex jam
descriptis satis liquet resistentiam corporum celeriter motorum
densitati Fluidorum. in quibus moventur proportionalem esse
quam proxime. Non dico accurate. Nam Fluida tenaciora, pari
densitate, proculdubio magis resistunt quam liquidiora, ut Oleum
frigidum quam calidum, calidum quam aqua pluvialis, aqua quam
Spiritus Vini.' He concludes that assumption (ii) holds 'satis
accurate' for liquids 'qui tam fluidi sunt ut in vasis agitati motum
impressum diutius conservent, effusique liberrime in guttas decur-
rendo resolvantur'.

   In spite of this discounting of the importance of viscous effects
in nature, he returns to the simplest assumption in section IX,
where he considers the rotation of fluids on the hypothesis:
'Resistentiam quae oritur ex defectu lubricitatis partium Fluidi,
caeteris paribus, proportionalem esse velocitati qua partes Fluidi
separantur ab invicem.' The whole theory and practice of vis-
cometry are based on this hypothesis.

3. Work of Coulomb, Navier and Stokes. The manifestation of
resistances proportional to the velocity was demonstrated by Cou-
lomb (1801) in the slow oscillations of a disk suspended by a torsion
wire in water and in oil. For a description and explanation of his
work see Brillouin, *Leçons*, §§ 5–16. Apart from Coulomb's memoir,
the experimental and mathematical investigations of a century and
a half provided no important advance in the concept of viscosity,
although there was matter in them which demanded explanation.
(For references see Chap. I of Bingham's *Fluidity and Plasticity*

and of Hatschek's *The Viscosity of Liquids*). Navier (1823), who first stated the general equations for motion in real, i.e. viscous, fluids as distinct from the ideal fluids of hydrodynamics, gave a definition of a constant appearing in his solution which is practically identical with that stated below for the coefficient of viscosity: similar solutions were obtained by Poisson (1831) and by Stokes. Stokes[3] made it quite clear that he considered 'the fluidity of water and other such fluids' to be 'not quite perfect' and that 'there is a whole class of motions of which the common theory (hydrodynamics) takes no cognizance whatever, namely, those which depend on the tangential action called into play by the sliding of one portion of a fluid along another or of a fluid along the surface of a solid or of a different fluid' (Stokes[4]). Since the formula which he obtained for the discharge from pipes did not agree with the data then available, which were for turbulent flow, he suggested that experiments with rotating cylinders, such as were made later by Couette, might furnish indications of the effect of the presence of a solid boundary on the velocity distribution deduced from his equations.

4. Definition of viscosity. Stokes's formulae for the flow of liquids in tubes were confirmed by Poiseuille's experiments (see next chapter), the results of which were shown by Wiedemann and by Hagenbach to be in accordance with an elementary application of Newton's hypothesis and to furnish reproducible values for the '(coefficient of) viscosity' of water and of other liquids. For this quantity the following definition may be used, which is due to Maxwell (the exact wording is taken from a pamphlet issued by the British Engineering Standards Association[5]): 'The coefficient of viscosity of a fluid is the numerical value of the tangential force on unit area of either of two parallel planes at unit distance apart when the space between these planes is filled with the fluid in question and one of the planes moves with unit velocity in its own plane relatively to the other.'

The mathematical expression of Newton's hypothesis is simply

$$F = \eta \, . \, dv/dx, \quad . \quad . \quad . \quad . \quad \text{(I. 1)}$$

where F is the force exerted by the fluid per unit area of a plane parallel to the direction of motion when the velocity is increasing with the distance x, measured normally to the plane, at the rate

dv/dx. The constant of proportionality, η, is the viscosity coefficient, the physical dimensions of which are thus $[ML^{-1}T^{-1}]$. Instead of the cumbrous expression 'C.G.S. unit of viscosity' or the abbreviation gm. cm.$^{-1}$ sec.$^{-1}$ for 'dynes per sq. cm. per unit velocity gradient', Deeley and Parr[6] proposed the term 'poise', in honour of Poiseuille: the suggestion has been almost universally adopted and the derived unit, the 'centipoise' (cp.), is commonly employed: the viscosity of water at $20°$ C. is $1·009$ cp. The reciprocal of the viscosity coefficient is known as the fluidity (ϕ) and has been claimed, particularly by Bingham, as a more rational basis of comparison than the viscosity itself in theoretical work on the constitution of liquids.

Stokes spoke of 'internal friction' rather than of viscosity, and the same phrase is still frequent in German writings. The word viscosity is not new, however; in Ben Jonson's *Alchemist*, Face, acting as Lungs or laboratory attendant to Subtle, says mercury may be known 'by his viscosity, his oleosity and his suscitability'.

The quotient of viscosity by density (η/ρ) assumes much importance in hydraulics and aerodynamics, and has received the name 'kinematic viscosity', usually abbreviated as ν. It has been suggested that the concept of kinematic viscosity should be regarded as the more fundamental, that of the ordinary or dynamical viscosity being derived from it, instead of vice versa. Kinematic viscosity has the dimensions $[L^2 T^{-1}]$, which are those of a coefficient of diffusion, and may be considered to connote the diffusion of momentum. Jakob[7] has proposed that the C.G.S. unit be called the 'stokes', but the suggestion has not yet had time to bear fruit.

5. Limits of applicability of the laws of viscous flow. The laws of viscous flow deduced from Newton's hypothesis have provided a foundation for the viscometry of the most diverse materials, from gases and mobile liquids like ether to substances like pitch and glass which, though apparently solid, may be shown to flow under very minute shearing forces. It is thus possible to measure and to define in absolute and reproducible units the viscous properties of any industrially important system, subject to one restriction which will be mentioned below. The possession of these methods of examination has stimulated the accumulation of a mass of data relating to the viscosities of pure liquids and solutions, the discussion of which still affords wide scope for

theoretical investigations into molecular complexity and its variation with temperature, pressure, dilution, &c. Some day, no doubt, consideration of such data will lead to the formulation of a unifying theory of the liquid state which will be as illuminating as the kinetic theory of gases or the more recent conceptions of the structure of crystals. The viscometry of gases provided one of the most brilliant verifications of the kinetic theory, and in the study of colloidal solutions the viscometer has proved itself invaluable, even when used in conditions which are now stigmatized as inadequately defined.

Reynolds's criterion (see Chap. II) imposes an upper limit on the velocity gradients which may be employed without changing the viscous flow of a fluid into a disordered or turbulent flow to which the simple laws do not apply. In the direction of decreasing gradients no such universal criterion has been discovered. Stokes remarked (1845) that 'there seems to be no line of demarcation between a solid and a viscous fluid. . . . The gradation of viscous into what we call perfect fluids seems to present as little abruptness as that of solids into viscous fluids', and 'a fluid admits of a finite but exceedingly small amount of constraint before it will be released from its state of tension by its molecules assuming new positions of equilibrium', but he regarded the constraint as 'probably insensible'. Attempts have been made to obtain evidence of such constraint in the case of water, by making determinations of the apparent viscosity at very low rates of shear: if water had any rigidity the viscosity calculated by the usual formulae would tend to increase at low velocities in fine capillaries. The most recent investigations in this direction are those of Griffiths and Griffiths[8] and of Griffiths and Vincent,[9] who showed that measurements in which the rate of shear at the wall was only 0·0017 radian per sec. gave values for the viscosity of water which agreed with those obtained by conventional methods, in which the rate of shear may be as much as 10^4 radians per sec.

Similar experiments have not yet been made with other pure liquids but discordances from the laws deduced on Newton's hypothesis have been observed at low rates of shear in the study of (i) very viscous liquids such as pitch at room temperatures, glass near its annealing temperature (see Chap. X § D), or solutions of colophony in turpentine (Glaser[10]); (ii) colloidal solutions, particularly such as will set to a jelly when cooled to lower

temperatures than that of the test or when used in higher concentration (see Chap. XI); (iii) systems consisting of two liquid phases or of a solid and a liquid phase.

The failure of the laws in the case of heterogeneous systems is hardly surprising since there must be disturbances of velocity gradient near each suspended particle. There is, of course, no sharp line of division between (ii) and (iii), though the particles in colloidal solutions may be submicroscopic or so nearly allied to the continuum as to be indistinguishable by other than viscometric means: lyophylic colloids seem to possess an extensive but sometimes weak structure. Very viscous liquids are usually supposed to contain highly associated, together with simpler, molecules and it is possible that under shear the degree of association varies so that extra resistance is offered. Evidence of orientation is obtainable in experiments on flowing 'crystalline liquids' and it is probable that high viscosities arise from a species of entanglement between long-chained complexes which may become more regularly arranged when subjected to continuous shear. It can scarcely be doubted that anomalies would be discoverable in the flow of liquids even so fluid as water if it were possible to make reliable measurements either in channels having diameters not very much greater than that of the sphere of action of the molecule of the liquid or at rates of shear so low as to produce a viscous drag which was small compared with the forces causing temporary association. Bingham's distinction (*Fluidity and Plasticity*, Chap. III) between 'diffusional' and 'collisional' viscosity is suggestive in this connexion.

Although it is only during the last fifteen years that any significant advance has been made towards an understanding of the nature of the flow of colloidal solutions, emulsions and suspensions, viscometric methods have been used empirically and fruitfully both in industrial and in purely investigational work on systems of the most diverse types. As will be more fully explained in Chapter XI, the indications thus obtained cannot yet be made absolute, i.e. independent of the particular viscometer employed; but in many cases the variations of apparent viscosity with nature of the solute or composition of the solvent are so large as to preclude the possibility of confusion. Thus Wo. Ostwald claims that the occurrence of a viscosity minimum for gelatine sols near the iso-electric point would be detectable by almost any viscometer.

6. The importance of temperature measurements in viscometry. It cannot be too strongly emphasized that data regarding viscosities should always be accompanied by a specification of temperature. The viscosities of gases at 0° C. may increase by as little as 0·2 per cent. per 1° C. rise in temperature, but those of liquids decrease at a more rapid rate; thus, for water at 100° C. ($\eta=0\cdot28$ cp.) the temperature coefficient is about -1 per cent. and at 0° C. ($\eta=1\cdot79$ cp.) it is $-3\cdot5$ per cent. As a rough general rule the effect of temperature is more marked the higher the viscosity; for castor oil at 20° C. ($\eta=986$ cp.) the rate of decrease is 8·4 per cent. per 1° C., while for a pitch at 20° C. ($\eta=3\times10^8$ poises) the figure becomes more than 30 per cent. The magnitude of these coefficients is sufficient to indicate the necessity for a precise regulation of temperature if concordance is to be obtained between duplicate tests in a given apparatus: it is also clear that, even when the accuracy of the thermometry is as high as is at present possible, the reproducibility of viscosity values determined in different laboratories cannot extend to as many significant figures as may reasonably be given for the values of such a property as density. The importance of the control and measurement of temperature is not laboured afresh in each of the descriptions of viscometric methods which follow, but must be borne in mind when preparing for any measurement.

The reader must be referred to general manuals of practical physics and physical chemistry for an account of thermostats suitable for different ranges of temperature. A practical hint in connexion with electric regulators having a mercury contact may, however, be mentioned, since, though well known, it has not found its way into many text-books. Sparking at the make-and-break between the mercury and a nichrome or platinum wire, which leads to fouling of the contact, may of course be minimized by reducing the voltage and self-induction in the regulator circuit —a procedure which generally involves the use of additional relays—but sparks which are quite vigorous in air are quenched by providing an atmosphere of hydrogen. A 100-volt circuit including a solenoid and operating a gas-tap or a 20-ampere switch may be interrupted at the regulator for months on end, by means of a Gouy type of contact oscillating about four times a minute, if a slow stream of hydrogen from a simple electrolytic generator be led past the contact: in air the mercury surface would become

dirty in a few minutes unless the sparks were quenched by other means.

REFERENCES

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THE VISCOUS FLOW OF FLUIDS IN TUBES

1. Introduction. The flow of liquids and gases in pipes and channels is an occurrence so common in daily life and of such importance in engineering design that it could hardly fail to engage the attention of scientists as soon as the cardinal principles of physics began to be studied by experiment and analysis. Hydrodynamics attracted the most eminent mathematicians of the eighteenth century, and much careful and practical investigation of the flow of water in pipes was carried out before the middle of the nineteenth century. But, as will be shown later, the laws governing the large-scale movements of water are of a very complicated nature and are only now beginning to be understood. It was not until attention was directed to the transpiration of liquids through tubes of very small cross-section that the relatively simple laws of viscous flow could be discovered

Although biophysics has made many valuable contributions to general physical science in recent years, it has provided no discovery so fruitful as that announced in 1840 by Poiseuille,[1] professor of physics in the Paris medical schools. With a view to obtaining some understanding of the laws governing the passage of the blood through the capillaries by which it is distributed through the body, he instituted a series of researches on the simplest analogue of which he could conceive, namely, the flow of pure water through the fine bores of thermometer tubing. By this simplification, made in accordance with the principles which have so often been adopted in modern experimental science, he was led to discover definite relationships between the rate of flow Q and (i) the pressure difference P between the ends of the tube, (ii) the length l and (iii) the diameter D of the tube. The results are summarized in the formula,

$$Q = k\frac{PD^4}{l}, \qquad (\text{II. 1})$$

where k is a constant; this empirical result, expressed in this and other forms, is known as Poiseuille's Law. It may be remarked, parenthetically, that the flow of blood through fine capillaries has since been found not to obey this law (see Chap. XI).

The concept of viscosity had scarcely been developed at this

time and Poiseuille went no further on the theoretical side than to show that the constant k of his formula was one which was characteristic of a given liquid at a given temperature. He determined the variation of k for distilled water between 0° C. and 45° C. and also made measurements on mixtures of alcohol and water to show the relation between k and the alcohol content.

The conclusions reached by Poiseuille were so simple and unexpected that his work and his methods were examined, as was then the practice of the Académie des Sciences, by an expert committee whose findings were reported[2] in 1842. They satisfied themselves of the accuracy and value of his work, and his memoir was printed *in extenso* in the *Receuil des savants étrangers* of 1846. It forms one of the classics of experimental science and is frequently quoted as a model of careful analysis of sources of error and painstaking investigation of the effects of separate variables. The original paper is somewhat inaccessible but the procedure is described in considerable detail by Brillouin[3] and, more summarily, by Bingham.[4] An appendix to Bingham's book gives details of all Poiseuille's measurements, tabulated for convenience of reference. In view of the availability of these descriptions to those who may be unable to consult the original I have deemed it sufficient to give here only the following brief mention of salient points of the work. A few of the precautions taken by Poiseuille to correct for certain small errors will be described in more detail when we deal with the use of present-day apparatus.

2. Poiseuille's experiments. The measurement which is most subject to error in all absolute determinations of viscosity by the capillary-tube method is that of the diameter of the capillary. The tubing used by Poiseuille was selected after a preliminary calibration by means of a thread of mercury, no tubes being incorporated in his apparatus which showed variations of more than 2 per cent. in the length of the mercury column at different positions or in which the variations were not fairly uniform. The mean diameters of the pieces finally chosen were determined by weighing the mercury which filled them: owing to the small bore (0·01 mm. in one case) it was necessary to combine several fillings of the same tube in order to avoid undue errors in weighing. In this method it is assumed that the tubes are right circular cylinders: the cross-sections of the ends were examined under the microscope to find

how far this assumption was warranted. The major and minor axes differed usually by less than 4 per cent., but in the widest tube, of 0·65 mm. bore, the variation amounted to 11 per cent. Since it was part of his programme to investigate the effect of the length of the tube, he was able to obtain some information as to the constancy of the ellipticity over the whole tube by repeating this examination on each fresh cross-section which became accessible as the tube was progressively shortened.

Poiseuille found that he could not measure with satisfactory accuracy the volume of water flowing through the capillary in a given time by allowing the tube to discharge through the air into a weighed vessel, since the delivery from fine tubes is not regular under such conditions. He decided to keep the down-stream end of the capillary submerged in the water of his constant-temperature bath and he was therefore obliged to measure the volume at the other end. For this purpose he attached a bulb to the capillary via a right-angle bend (see Fig. 1): the capillary was arranged to lie horizontally in the bath, and the time was observed which was required for the water meniscus to fall from a mark made just above the bulb to one just below it. The volume comprised between these two marks
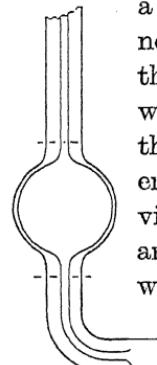
FIG. 1.   Poiseuille's viscometer.

was determined by weighing; in one case it was as small as 0·125 cm.³ The small bulb shown between the measuring bulb and the capillary represents a seal made to the periphery of the latter in such a manner as to leave an abrupt end from which the length of the capillary might be measured. A vertical continuation of the tubing forming the upper end of the measuring bulb was sealed into the side of a pear-shaped glass vessel of which the pointed end, projecting downwards below the junction, was intended to serve as a trap for dust, &c. This vessel could be connected either to a suction pump, by means of which liquid could be sucked from a storage bottle through the capillary to fill the bulb, or, in the actual experiment, to a 50-litre copper reservoir into which air was pumped, the pressure being measured by a mercury or water manometer. Appropriate corrections were applied to the pressure indicated by the manometer to allow for the effects of the varying hydrostatic head in the viscometer, for

capillarity, &c. With the details of such corrections we shall deal in a later section. The main series of experiments were made at 10° C., the temperature of the bath in which the capillary and bulb were immersed being maintained constant within about 0·05° C.

Measurements were made of the rate of efflux through thirteen different capillaries, of which the diameters varied between 0·013 mm. and 0·65 mm., the pressure being varied over the range 5 mm. to 10 metres of mercury. The original lengths of the capillaries were in some cases nearly one metre, but when one series of tests was completed the lengths were gradually reduced, sometimes in as many as ten stages, and the experiments on the effect of pressure repeated on each new length in more or less detail. Several different determinations were also made of the effect of temperature, between 0° C. and 45° C.

From the mass of data thus accumulated Poiseuille was able to show that, with certain limitations, the rate of discharge of water through a capillary is given by formula (II. 1) with an accuracy of 0·1 to 0·2 per cent. It is important to note that the constant k is independent of the dimensions of the viscometer; it varies only with the nature of the liquid and with the temperature. No formula of such simplicity and generality has even yet been obtained for flow in wider tubes.

The proportionalities indicated by formula (II. 1) were observed by Poiseuille to become inexact when the length of the tube was reduced, i.e., with a given diameter, when the velocity of the flow was increased. He gives a table showing the lengths of tubing of various diameters below which his law of pressures ceases to hold: the table shows that the wider the tube the greater is the ratio of this critical length to the diameter. These and similar observations have led to a number of attempts being made by various workers to extend the range and increase the accuracy of Poiseuille's law by the introduction of corrections for the effects of the ends of the tubes: these corrections form the subject of sections 4 to 6 of this chapter.

3. Deduction of Poiseuille's Law from theory.
In a long paper read in 1845, dealing with 'the theories of the internal friction of fluids in motion' Stokes[5] deduced the equations of motion of a viscous liquid in contact with a solid. He gave, *inter alia*, a formula for the distribution of velocities across the section of a

long straight pipe through which a fluid flows in virtue of a pressure head determined by the slope of the pipe. He presumably integrated a more general equation of the same type and must thus have obtained Poiseuille's Law mathematically, for he states that he calculated the discharge from long pipes but arrived at formulae which did not agree with the experimental results of Bossut and Dubuat; these workers had carried out accurate measurements, using tubes and channels of much greater width than Poiseuille's capillaries. Stokes did not publish the discharge formula but he realized that it should be possible to prove the presence or absence of slip at the walls of the pipe by suitable experiments on the rate of flow.

The first published deduction of Poiseuille's Law was by Wiedemann[6] but it was given in a more precise form by his pupil Hagenbach[7] four years later. They assumed (*a*) that the viscous resistance varies as the relative velocity of adjacent layers of liquid, and (*b*) that there is no slip of the liquid in contact with the wall of the tube. A somewhat similar deduction was made by Neumann in his lectures on Hydrodynamics about the same time, but the lectures were not printed until after Hagenbach's paper had appeared. Hagenbach's proof involves certain unnecessary assumptions regarding the molecular constitution of fluids, but his method is virtually the same as that used in modern text-books of physics. Though the calculation is familiar to most physicists no apology is offered for reproducing it here.

Consider a right cylindrical tube of radius a and length l through which a fluid is driven by the application of a pressure difference P between the ends. It is assumed: (1) that the flow is everywhere parallel to the axis of the tube; (2) that the flow is steady, initial disturbances due to accelerations from rest having been damped out; (3) that there is no slip at the walls of the tube, i.e. the fluid in contact with the wall is at rest; (4) that the fluid is incompressible; (5) that the fluid will flow when subjected to the smallest shearing force, the viscous resistance being proportional to the velocity gradient.

It follows from assumptions (1), (2) and (4) that the velocity u of any infinitely small portion of the fluid is constant in direction and magnitude from one end of the tube to the other. From assumptions (1) and (5) it follows that the pressure is uniform across any cross-section of the tube, otherwise there would be some radial

component of velocity or some elastic deformation of the fluid. Hence the pressure gradient dp/dl is constant, or, since the pressure decreases by P from the entrance to the exit end,

$$\frac{dp}{dl} = -\frac{P}{l}.$$

Let us evaluate the forces acting on a small portion of the fluid comprised between two cylindrical surfaces, coaxial with the tube, having radii r and $r + \delta r$, and terminated by planes unit distance apart at right angles to the axis.

The fluid nearer to the axis than r exerts a shearing force on each unit of area of the inner surface of the annular cylinder equal to $-\eta \dfrac{du}{dr}$ tending to drag the element of fluid in the direction of u.* The whole area of the unit length of this surface being $2\pi r$, the viscous force tending to accelerate the element of fluid considered is

$$-2\pi r \ \eta \frac{du}{dr}.$$

Similarly, the fluid external to the outer surface of our imaginary annular cylinder exerts a force tending to retard it equal to

$$-2\pi \eta \left\{ r\frac{du}{dr} + \delta r \cdot \frac{d}{dr}\left(r\frac{du}{dr} \right) \right\}.$$

The net viscous force tending to reduce the velocity of the unit length of cylinder is thus

$$-2\pi \eta \frac{d}{dr}\left(r\frac{du}{dr} \right) . \delta r.$$

Since the velocity is steady, this force must be equal and opposite to that due to the effect of the fall in pressure over the unit length considered. The force due to this difference in pressure acting on the two plane ends of the annular cylinder is obviously $2\pi r . \delta r . \dfrac{P}{l}$ acting in the direction of u;

$$\therefore \quad 2\pi \eta \frac{d}{dr}\left(r\frac{du}{dr} \right) . \delta r = -2\pi r . \delta r \frac{P}{l}.$$

Hence

$$\frac{d}{dr}\left(r\frac{du}{dr} \right) = -\frac{Pr}{\eta l}.$$

After two integrations this becomes

$$u = -\frac{Pr^2}{4\eta l} + A \log r + B, \quad . \quad . \quad . \quad \text{(II. 2)}$$

where A and B are constants.

* Assumption (3) leads us to suppose that du/dr is negative.

Since the velocity is not infinite at the axis, $A = 0$. The condition that the velocity must be zero at $r = a$ gives

$$u = \frac{P}{4 \eta l}(a^2 - r^2), \quad . \quad . \quad . \quad . \quad . \quad \text{(II. 2 a)}$$

so that the distribution of velocities is a parabolic function of the radius.

The quantity of liquid passing through any annular cross-section of the tube per second is obviously $u \,.\, 2\pi r \,.\, dr$. Hence the total volume Q flowing through the tube in unit time is given by

$$Q = \int_0^a u \,.\, 2\pi r \,.\, dr = \frac{2\pi P}{4\eta l} \int_0^a (a^2 - r^2)\, r \,.\, dr$$

$$= \frac{\pi a^4 P}{8 \eta l} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II. 3)}$$

Thus the constant k of Poiseuille's empirical formula (II. 1) is equal to $\dfrac{\pi}{128\,\eta}$.

Hagenbach made some experiments himself to check the truth of the above equation (II. 3) and found, as Poiseuille had done, that it held for low velocities of flow but became subject to error as the diameter of the capillary was increased or its length decreased. The measurements were considerably less accurate than those of Poiseuille; the method of experiment was also essentially different, the water being contained in a tank 2 ft. high, from the bottom of which the capillary protruded horizontally into the air. The rate of discharge was determined by weighing the amount of water caught in a recipient in a given time. The fact that the efflux took place into air instead of into a reservoir of water constitutes a variation from Poiseuille's procedure which is of some importance, this being the condition to which refers Hagenbach's correction for velocity head, with which we have next to deal.

4. The kinetic-energy correction. In his deduction of Poiseuille's Law, Hagenbach recognized that the excess, P, of the pressure at the entrance end of the tube over that (of the air in his experiments) at the exit end was due partly to a velocity head and partly to a resistance head; the former, h', was supposed to be the head corresponding, on Bernoulli's theorem of continuity, with the velocity of efflux and the latter, h'', the head necessary to

supply the work dissipated or converted into heat by the viscous forces. For long and fine tubes h' will be negligible compared with h'', and it is in fact neglected in the above derivation. In order to allow for the velocity head it becomes necessary to consider the equations for the energy of the system, or, since the liquid is in motion, for the rate of supply and of expenditure of energy.

Hagenbach reasoned that if there were no friction, and the flow occurred under a head h', the velocity of efflux would be $\sqrt{2gh'}$; hence the kinetic energy of the liquid flowing through the tube per second would be

$$\tfrac{1}{2}\pi a^2 \rho \sqrt{2gh'} \times 2gh'.$$

By equating this expression to the actual kinetic energy possessed by the liquid, calculated in the same manner as is set out below, he obtained a value for the velocity head h' to be subtracted from the total head to give h''. He thus found

$$h''\rho g = P - \frac{\rho}{\sqrt[3]{2}} \cdot \frac{Q^2}{\pi^2 a^4}.$$

When the above correction was applied to Poiseuille's results, Hagenbach found that he could deduce values of η which were constant up to considerably higher velocities than those at which the simple law failed.

A flaw in Hagenbach's argument was pointed out by Wilberforce,[8] who remarked that the pressure required to produce a certain kinetic energy must depend on the volume of liquid actually issuing. It is therefore not permissible to deduce the velocity head from a hypothetical rate of discharge. Wilberforce explained the treatment now accepted, which may be stated as follows:

The work expended in moving a volume of liquid $Q \cdot dt$ from the reservoir, in which the pressure is P above that at the exit end of the capillary, to a region where the pressure is equal to that at the exit end is obviously equal to $P \times Q \cdot dt$.

The kinetic energy imparted to the liquid per second on entering the capillary from a reservoir supposed to be of infinite area, and retained by the liquid until it leaves the tube, is the sum of the kinetic energies calculated for the elements of liquid which pass any cross-section of the tube per second. Now through any small annulus of mean radius r and width dr in a given cross-section there flows a volume of liquid $u \cdot 2\pi r \cdot dr$ per second, where u is

given by equation (II. 2a) above. The kinetic energy of this volume of liquid is

$$\tfrac{1}{2}\rho u \,.\, 2\pi r \,.\, dr \times u^2.$$

The kinetic energy of the liquid flowing through the whole of the cross-section per second is thus

$$\int_0^a \pi\rho u^3 r \,.\, dr \;=\; \pi\rho\left(\frac{p}{4\eta l}\right)^3 \int_0^a (a^2-r^2)^3 r \,.\, dr$$

$$=\; \pi\rho\left(\frac{p}{4\eta l}\right)^3 .\, \frac{a^8}{8}\,,$$

where p is the effective pressure difference used in overcoming the viscous resistances. Introducing Q, as in equation (II. 3), this kinetic energy becomes

$$\frac{\rho Q^3}{\pi^2 a^4}\,.$$

The total work expended per second must be equal to the work done against the viscous forces plus the kinetic energy retained by the liquid when it leaves the capillary. The work done against the viscous forces in each second is thus

$$PQ- \frac{\rho Q^3}{\pi^2 a^4}\,.$$

The pressure p effective in overcoming viscous resistance is therefore given by

$$p \;=\; P- \frac{\rho Q^2}{\pi^2 a^4}\,. \qquad . \quad . \quad . \quad . \quad . \quad \text{(II. 4)}$$

This expression differs from that obtained by Hagenbach in the omission of the numerical factor $(2)^{-1/3}$.

The correction deduced above was also found independently by Couette[9] a year earlier. It had actually been derived by Neumann before Hagenbach's paper appeared and by Finkener before 1890, but the proof had remained unpublished, and various factors, ranging from Hagenbach's 0·79 to Reynolds's 0·5, had been suggested and used to modify the term $\rho Q^2/\pi^2 a^4$. It will be convenient to refer to the factor or coefficient of the 'kinetic-energy' term as m; thus, according to Couette and Wilberforce $m = 1·0$.

The substitution by which Q was introduced in the above deduction of the kinetic-energy correction tacitly involves assumption (2) made in § 3 in the derivation of equation (II. 3). It is obvious that in the immediate vicinity of the up-stream end of the tube this assumption must be incorrect, since the liquid leaving

the reservoir, in which its velocity is supposed to be negligible, is here accelerated until the parabolic distribution of velocities, characteristic of viscous flow in a long tube, is established. The mathematical treatment of the flow under such conditions is considerably more complicated than for the steady state with which we have hitherto been concerned. It was given by Boussinesq[10] in a series of papers which appeared about the same time as those of Couette and Wilberforce. Briefly, the argument is as follows: If the mean rate of discharge were established without friction, giving a velocity $v = Q/\pi a^2$ uniform over the whole cross-section of the tube, the fall in pressure due to this acceleration of the fluid from rest would be $\frac{1}{2}\rho v^2$, by Bernoulli's principle. The fact that the velocity distribution is not uniform but parabolic, the fluid at the axis having a velocity $2v$, necessitates a further loss of head corresponding with a fall in pressure which is also equal to $\frac{1}{2}\rho v^2$. The parabolic distribution is that which necessitates the least work being done against the viscous resistances, so that in those sections of the tube nearer to the entrance, where the velocity distribution is more nearly uniform, a larger pressure gradient exists than in subsequent sections. The total amount of the extra pressure drop due to this cause, integrated from the actual entrance up to a region where the normal distribution of velocities has been established, works out, on a first approximation, to $0.12\,\rho v^2$. Boussinesq thus arrives at the result $m = 1.12$.

In defining the conditions assumed in his derivation of this result, Boussinesq states that the tube is supposed to be *bien évasée*, so that the filaments of liquid issuing from the reservoir into it fill it completely and become practically rectilinear and parallel immediately. This assumption of a rounded orifice is necessary for the application of Bernoulli's principle. But Boussinesq has very frequently been cited as authority for the use of the coefficient $m = 1.12$ under conditions foreign to this assumption; thus, his value has been applied to cases in which, in order to obtain an accurate measurement of the length of the capillary, the ends have been carefully polished to make the transition to the bore as abrupt as possible.

The last of the series of papers by Boussinesq above cited contains an estimate of the length of that part of the tube over which the disturbing influence of the orifice of entry extends. Characterizing the velocity distribution across any section by the

ratio of the maximum to the average velocity, he suggests that the disturbance may be considered to have become negligible when this ratio is within 1 per cent. of the constant value, 2, which may be shown to occur in very long tubes. On this criterion he finds that the effect of the entrance extends over a length x_1, given by

$$\frac{x_1}{d} = 0\cdot065\,R, \quad . \quad . \quad . \quad . \quad \text{(II. 5)}$$

where d is the diameter of the pipe and $R = vd\rho/\eta$. If a deviation of 10 per cent. from the steady velocity distribution be supposed to cause a negligible increase in resistance, the disturbance is shown to be suppressed by the shorter length x_{10}, where

$$\frac{x_{10}}{d} = 0\cdot029\,R.$$

Since it is known (see later, § 7) that experiments in which the velocity of flow is such as to make R exceed 2,000 are in general unsuitable for the calculation of viscosities, these estimates provide some theoretical indication of what must be the minimum length of a tube in order that Poiseuille's formula, including a correction for kinetic energy, may be applied. A more definite limit has been calculated by Schiller,[11] who gives the length necessary as

$$\frac{x}{d} = 0\cdot029\,R. \quad . \quad . \quad . \quad . \quad \text{(II. 6)}$$

Schiller bases his mathematical treatment of the conditions of flow prevailing in the earlier portions of the tube on the assumptions:

(1) that, at the junction of the tube with the reservoir from which the liquid is being run off, the velocity is uniform all over the cross-section: this condition is considered to be realized if the tube is provided with a bell-mouth;

(2) that, in the middle of each cross-section thereafter, there is a circular area over which the velocity is uniform and higher than at the entrance: from the edge of this circle the velocity decreases according to a parabolic law, becoming zero at the wall. The area of the circle over which the velocity is uniform decreases as the section is taken further from the entrance, until eventually it disappears, the distribution being thenceforward parabolic right across the tube, as in ordinary stream-line flow.

These assumptions enable him to calculate the drop in pressure due to the transition from the uniform to the parabolic distribution, and hence the value of m, which he finds to be $1\cdot08$ (see p. 32).

5. The Couette correction. The liquid entering the capillary and there acquiring a certain velocity must be supposed to be flowing in a converging stream from the wider supply vessel. Any differences in velocity between adjacent filaments in this stream will then involve the expenditure of work in overcoming viscous resistance; such differences in velocity appear to be a necessary consequence of the drag produced by the presence of the plane ends of a thick-walled capillary which has been cut and ground off at right angles to its axis. Couette[12] was the first to suggest the need for a correction to Poiseuille's Law to allow for this external resistance, and since he also made attempts to estimate its amount, the correction is known by his name. It may be shown (cf. Brillouin)[13] that the effect of the resistance in the converging stream-lines may be expressed in terms of a hypothetical addition λ to the length of the capillary, λ being proportional to the radius. The value of the constant $n = \lambda/a$ has been calculated for the analogous case of the end correction for the conduction of electricity in a cylinder opening into an infinitely wide cylinder of the same material (Maxwell,[14] Rayleigh[15]). Rayleigh's value $n = 0.824$ (for one end) was checked by Schrader[16] by measurements of the electrical resistance of mercury in a glass tube and of potassium bisulphate in an ebonite tube, which gave $n = 0.805$.

6. Experimental determination of the 'kinetic-energy' and Couette corrections. When the original Poiseuille equation (II. 3) has been modified by the insertion of the above corrections, it becomes

$$\eta = \frac{\pi a^4 P}{8 Q (l + na)} - \frac{m \rho Q}{8 \pi (l + na)}, \quad . \quad . \quad . \quad (II. 7)$$

the symbols having the connotations already explained. Many investigations have been made with the object of determining the values of the constants m and n by experiment, since it has been realized that some, at least, of the simplifying assumptions made in the theoretical derivation of the equation may be violated under the conditions prevailing in the practical measurement of viscosity. In some of the methods employed in the analysis of the experimental data the values have been more or less interdependent; hence it will be convenient to discuss both together.

(a) *Analysis of Poiseuille's data: Knibbs's methods.* Couette[17] examined Poiseuille's results for two short tubes in which the

product of pressure and time of flow of a given volume of water was no longer constant. Applying a kinetic-energy correction with $m = 1$, he found that each tube gave practically constant values for the viscosity provided the velocity was not too high, but that the value so obtained with the shorter tube was some 2·6 per cent. higher than that given by the longer tube of the same diameter. The lengths of the two tubes were respectively 0·68 cm. and 1·57 cm., so he assumed that the virtual addition na to the lengths, caused by the resistance external to the tubes, was given by the relation

$$\frac{0\cdot68+na}{1\cdot57+na} = 1\cdot026 \times \frac{0\cdot68}{1\cdot57}.$$

The radius of the tubes being 0·0071 cm., n is thus found to be about 5. Couette also made experiments himself, using tubing having a radius seven times as great, from which he deduced the value $n = 6\cdot4$.

There is no very good reason for confining the analysis of Poiseuille's data to only one of the capillaries used by him, when he gives results obtained by progressively shortening at least six of his tubes. Further, the average value assumed for the apparent viscosity, corrected only for kinetic-energy losses, depends on the actual coefficient m used in making that correction. Knibbs[18] reviewed the available data very much more comprehensively, introducing for the purpose a graphical method of representing them which has been widely used by subsequent workers. The modified Poiseuille equation (II. 7) may be written as

$$\eta = \frac{\pi a^4 h \rho g t}{8\,V\,(l+na)} - \frac{m\rho V}{8\pi t\,(l+na)}, \quad . \quad . \quad \text{(II. 7 a)}$$

by replacing P by $h\rho g$, where h is the head expressed in terms of the liquid of density ρ in the viscometer, and putting $Q = V/t$ where V is the volume discharged in time t. Knibbs pointed out that, for any series of results obtained for one liquid at a fixed temperature but with varying heads, this equation may be rearranged to read

$$C + \frac{c}{t} = h\rho t, \quad . \quad . \quad . \quad . \quad \text{(II. 8)}$$

where $C = \dfrac{8\,\eta V l}{\pi a^4 g}\left(1+n\,\dfrac{a}{l}\right)$ and $c = \dfrac{m\rho V^2}{\pi^2 a^4 g}.$

For a given viscometer, for which V, l, and a are constants, C and

c are also constants, so that the equation is that of a straight line if $h\rho t$ be plotted against $1/t$. The straight line fitted to the experimental data will then intersect the axis of ordinates at a distance C from the origin and will make an angle $\tan^{-1}c$ with the axis of $1/t$. If the points agree well with the linear relationship, it may be assumed that m is strictly constant for the given tube and that its value is given by the above definition of c. This procedure eliminates the error caused by the use of a possibly incorrect theoretical value for the coefficient of the kinetic-energy term, and enables results to be included which have been obtained under conditions such that the kinetic-energy loss forms a considerable fraction of the total fall of pressure between the vessels with which the capillary communicates.

In order to deduce the value of n from the data of Poiseuille relating to the flow of water at $10°$ C. through various capillaries, C is found for each viscometer by the above method, and the definition of C is rewritten

$$\frac{\pi a^4 g C}{8 Vl} = \eta\left(1 + n\frac{a}{l}\right).$$

The left-hand side of this equation, which may be abbreviated as K, is still a constant for a given capillary; η need not be supposed to be known, but it may be assumed to be constant from one experiment to another, so long as the temperature and the nature of the liquid remain the same. Hence, if K be plotted against a/l, the points obtained should lie on a straight line, intersecting the K axis at $K = \eta$ and making an angle $\tan^{-1}n\eta$ with the axis of abscissae. The graph of $h\rho t$ against $1/t$ therefore enables us to find, by extrapolation, the value of $h\rho t$ which corresponds with infinitely slow flow through each capillary, and the graph of K against a/l gives, by a similar extrapolation, the value of η which corresponds with the flow through a tube of infinite length. In other words, the kinetic-energy correction and the Couette correction have both been applied, using the coefficients appropriate to the experimental conditions. The slope of the second graph, together with the final estimate for η, allow n to be evaluated.

From an examination of the whole of the pertinent data of Poiseuille, Knibbs found that the mean value of m indicated by these experiments is 1·14, but that the variations were consider-

able in different series. The two extreme values, 0·4 (which depends on a straight line drawn through three points only) and 1·87 (which may conceivably have been due to partial obstruction of the capillary), were neglected in the derivation of the mean, but those averaged ranged from 0·8 to 1·3. Knibbs analysed also some results due to Jacobson (1865): the mean obtained was again $m = 1·14$, but he remarked that not only does m appear to vary with different tubes but results from one tube in different experiments by Jacobson pointed to a variation from $m = 1·25$ to $m = 1·55$.

Knibbs was unable to confirm Couette's estimate of the value of n. The values obtained for Poiseuille's capillaries by the above graphical method were found to be as often positive as negative. The variations are probably due to the unavoidable inaccuracy in the determinations of the bore.

(b) *Hosking's experiments.* Some careful determinations of the viscosity of water were made by Hosking[19] in which the flow was increased from a moderate rate to one such that the kinetic-energy correction became nearly equal to the viscosity. These experiments were therefore very well adapted to the determination of m. Four capillaries were used and the value of m was found for each by Knibbs's method for flow both from right to left and from left to right. The values varied from 1·130 to 1·216, and differences as high as 0·05 occurred when the direction of flow was reversed. The modified Poiseuille formula gave approximately constant values for the viscosity of water at 50° C. ($\eta = 0·55$ cp.) until the kinetic-energy correction amounted to 55–60 per cent., when the curve $\rho ht = f(1/t)$ showed a sudden break. These results indicate that m remains constant, though different for each tube, until Reynolds's criterion attains a value of about 2,500. The lengths of the tubes ranged from 135 to 170 times their diameter, and the Couette correction appeared to be zero. The ends of the tubes had been ground flat in a lathe, and they projected well into relatively large spherical bulbs.

(c) *Herschel's method.* Experiments with capillaries suitable for the determination of the viscosity of liquids as mobile as water in the usual type of apparatus are not well adapted for the purpose of studying the Couette correction, since the ratio of length to diameter requires to be high in order to make the viscous resistance

predominate. The correction is deduced from the difference in resistance of tubes of different lengths, and even if the shorter of two tubes were 100 times and the longer 1,000 times the diameter, a value $\lambda = a$, i.e. $n = 1$, would represent a difference of only 0·45 per cent. in the uncorrected viscosities calculable from the two series of experiments. In order to allow a larger margin for error it is necessary to use more viscous media and shorter tubes, even though it may not be possible to determine the actual viscosities with the highest accuracy under such conditions.

The commercial viscometers employed in the examination of lubricating oils, &c. (Chap. IV) have outlet tubes of which the length is only some seven times the bore. The standardization of these instruments by finding the velocity of flow of oils of known viscosity offers an opportunity for ascertaining the limits of applicability of equation (II. 7) and for evaluating the constants m and n of the correction terms. The viscosities of the liquids used for calibration are obtained, directly or indirectly, from observations made in viscometers possessing capillaries so long that the corrections are small. Herschel[20] has devised a method of plotting the results of such tests which allows the two constants to be derived from one diagram when the necessary dimensions are known. The principle of the construction is as follows:

Let the viscosity which would have been calculated from an experiment by means of the uncorrected Poiseuille equation be denoted by η'. Then the relative error ϵ so introduced is given by

$$\epsilon = \frac{\eta'}{\eta} - 1 = \left\{ \frac{l + na}{l} \cdot \frac{P}{P - m\rho v^2} - 1 \right\},$$

where $v = Q/\pi a^2$. This expression is derived by comparing equations (II. 3) and (II. 7) and it may be rewritten

$$\epsilon = \frac{na}{l} + \frac{m\rho v^2 (l + na)}{l (P - m\rho v^2)}.$$

Let us introduce R into this equation from the relation

$$R = \frac{v d\rho}{\eta} = \frac{32 v^2 \rho (l + na)}{d (P - m\rho v^2)},$$

where η has been replaced by the corrected value derived from equation (II. 7). We thus obtain

$$\epsilon = \frac{na}{l} + \frac{md}{32 l} R \quad . \quad . \quad . \quad . \quad (\text{II. } 9)$$

Herschel makes use of the dimensions of the tube to obtain a

series of corresponding values of ϵ and R from the rates of flow of different liquids through it. Equation (II. 9) shows that when these values are plotted the points should lie on a straight line if m and n are constants. If the straight line is found to be inclined at an angle θ to the axis of relative errors, the numerical value of m is obviously

$$m = \frac{32\,l}{d\,.\,\tan\theta}.$$

Further, if the straight line when produced to $R = 0$ intersects the axis of relative errors at $\epsilon = \epsilon_o$, then

$$n = \frac{l}{a}\epsilon_o.$$

For two Standard Saybolt viscometer jets, having lengths 1·235 and 1·230 cm. and bores 0·1759 and 0·1770 cm. respectively, Herschel[21] found $n = 0\cdot62$ and 1·11. The value of m was 0·989.

By the same method the flow through the jet of a Redwood instrument was found to require $n = 0\cdot12$ and $m = 0\cdot953$ (Herschel[22]). A value $n = -1\cdot0$ estimated from his diagram for a jet which was 0·964 cm. long, and of which the diameter was taken as 0·1583 cm., is probably due to irregularity of the bore of the agate, a defect from which many of the older instruments suffered.

The slightly tapering jet of an Engler viscometer gave $n = 1\cdot4$ and $m = 1\cdot03$ (Herschel[20]). He has also examined the Ubbelohde modification of the Engler instrument, in which the length of the jet is 24 times its bore: here $n = 0\cdot3$ to 1·0, and $m = 1\cdot18$ to 1·11 (Herschel[23]).

(d) *Couette's method.* A method was suggested and used by Couette[24] by which the end-corrections might be eliminated and eventually estimated. The principle has recently been employed by Erk[25] in the design of a viscometer adapted for absolute measurements. A diagram of Erk's arrangement is shown in Fig. 10, p. 55: it differs from Couette's chiefly in the smaller size of the vessels B, C, D to which the manometers are attached, a detail which is valuable in that it allows the whole apparatus to be immersed in a thermostat. The idea involved is that the disturbing effect of the conditions at the ends of a capillary, through which a liquid is flowing at a given rate from one reservoir to another, extends only to a certain distance along the tube. Hence

the tube may be divided into (i) a certain central portion, of length $(l_1 - l)$, say, in which the pressure-gradient is that necessary to produce the given rate of flow through a tube of infinite length, and (ii) two terminal portions, of combined length l, in which the conditions of flow are affected by the proximity of the ends. The total fall in pressure, P_1, between the two reservoirs is thus equal to $(l_1 - l)\Pi + p$, where Π is the constant pressure-gradient in the central portion and p the fall due to the end portions. Now let the second reservoir be connected, by another capillary of exactly the same diameter but of length l_2, with a third reservoir so that the liquid flows through both capillaries at the same rate. Then if the ends of the two tubes are geometrically similar and are similarly disposed with respect to the reservoirs, it follows that the same pressure drop p will occur over terminal portions of combined length l in the second capillary. The total fall in pressure P_2, between the second and third reservoirs will thus be $(l_2 - l)\Pi + p$, the pressure-gradient Π being the same in the central portions of both capillaries since the rate of discharge and the diameter are unchanged. The values of Π and of p are not directly measured, but if the pressure differences P_1 and P_2 are observed we have

$$P_1 - P_2 = (l_1 - l)\Pi + p - (l_2 - l)\Pi - p,$$

$$\therefore \quad \Pi = \frac{P_1 - P_2}{l_1 - l_2}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II. 10)}$$

The effects of the ends are thus eliminated, and if the rate of discharge is measured the viscosity may be calculated by means of the uncorrected Poiseuille equation (II. 3), which applies strictly to a tube of infinite length, by substituting this value of Π for the P/l of that equation.

The fully corrected value so obtained for the viscosity may be introduced into equation (II. 7) together with the measured quantities P_1 and l_1 (or P_2 and l_2). Taking $m = 1.0$, Couette thus deduced $n = 6$ from one of his experiments: but a lower value for n would be obtained by assuming $m = 1.12$.

Bingham and White[26] modified this method of Couette's in an attempt to obtain a more definite value of n. They determined the times of flow of a given volume of water under similar heads through a capillary of length 9·4 cm. and radius 0·014 cm., before and after breaking the tube into 2, 3, 4, and 6 parts. The broken pieces were fitted into glass tubing with rubber joints. Assuming

that the end-corrections for each portion of the divided capillary were the same as for the original length and that $m = 1 \cdot 12$, they calculated from each observation the increase in the effective length due to subdivision. The values deduced for n varied irregularly from 0 to $0 \cdot 7$, but owing to the dimensions employed such variations were almost within the error of experiment and the use of a smaller coefficient for the kinetic-energy term would have given appreciably larger entrance corrections.

(e) *Bond's experiments*. The same principle underlies an investigation of the end effects made by Bond.[27] His method of experiment consisted in allowing various solutions of glycerol in water to flow from a wide vertical tube through a capillary into a beaker in which the outlet was submerged. The rate of fall of the level of the liquid in the wide tube was timed and, the volume corresponding with certain graduations being known, the results were plotted on a curve showing the rate of discharge at different heads. This procedure was repeated with the same solutions after replacing the capillary by another of the same bore but of different length. From the curves obtained the heads which produced the same rate of discharge through the two tubes were deduced. The observations are not tabulated in Bond's paper but are expressed by a graph (Fig. 2) in which the dimensionless quantities $y = \dfrac{Q}{a^2}\sqrt{\dfrac{P}{p_e}}$ and $x = \sqrt{\left(\dfrac{Q\rho}{a\eta}\right)}$ are plotted against one another. The end-correction p_e is defined by the equations $p_e = P_1 - \Pi l_1 = P_2 - \Pi l_2$, in which the remaining symbols have the same significance as in the last section: it will be noted that p_e differs from the quantity p there used. The values of ρ and of η were determined in separate experiments.

By comparing the above definition of p_e with equation (II. 7) it is seen that

$$p_e = \frac{8Q\eta}{\pi a^4} na + \frac{m\rho Q^2}{\pi^2 a^4}.$$

Substituting the definitions of the quantities plotted, we obtain

$$\frac{\pi^2}{y^2} = m + \frac{8\pi n}{x^2}.$$

The abscissae are connected with the Reynolds's numbers by the relation $R = 2x^2/\pi$.

From the origin up to a value of the abscissa corresponding with $R = 10$, Bond's curve is a straight line making an angle $\tan^{-1}c$ with the x-axis: if we interpret this result in terms of the above equation we must conclude that $m = 0$ and $n = \dfrac{\pi x^2}{8 y^2} = \dfrac{\pi}{8 c^2}$. The slope found by Bond corresponded with $n = 1\cdot132$: from some earlier experiments on viscous flow through an orifice plate he obtained a second estimate $n = 1\cdot160$, the mean being $n = 1\cdot146$.

Bond suggests the following interpretation of Fig. 2:

(i) the part (a), (b), (c) of the curve corresponds with the flow being purely viscous not only in the capillaries but in the wide reservoirs at each end:

(ii) the part (d), (e), (f) corresponds with the flow in the tube being viscous, but the end-correction being due to kinetic energy, so that turbulence occurs in the down-stream reservoir: the ordinate A represents $m = 1$ (and $n = 0$);

(iii) the portion (g) represents incipient turbulence in the tube, and the portions (h), (i) turbulence both in the tube and on emergence: the ordinates C and D give the range of values usually quoted for the end effect for wide pipes.

Dorsey[28] has made a critical study of Bond's results and remarks on the behaviour of a stream of water coloured by a dye when discharging from a capillary tube into a wide reservoir. At the lowest velocities the emerging dye forms a hemispherical cap seated on the plane end of the capillary. When a certain velocity has been reached the cap develops a stem and then the stem lengthens and the cap becomes larger as the velocity is increased: the rim of the mushroom-shaped figure takes on the appearance of a vortex ring, the whirls of which become more and more pronounced until their development is impeded by the surface of the water or by the walls of the reservoir. In the entrance reservoir there is no sign of any change in the distribution of the lines of flow as the velocity is varied. He concludes that up to $R = 10$ the flow is everywhere laminar, the end-correction given by $n = 1\cdot146$ and $m = 0$ representing the sum of the equal effects of the converging and diverging stream-lines at the two ends of the tube. He identifies the velocity at which the hemispherical cap of dyed water first develops a stem as that corresponding with $R = 10$ and suggests that above this point the effective length of the tube is increased only by half the above amount, i.e. $n = 0\cdot573$, owing to the converging stream-

lines at the entrance. At the outlet end the issuing jet of liquid carries away energy which is eventually dissipated as heat by the production of eddies that perform work against viscous forces in the reservoir: the work done outside the capillary may be represented by a kinetic-energy correction of conventional form with $m = 1$. As a matter of nomenclature, he stresses the fact that 'the
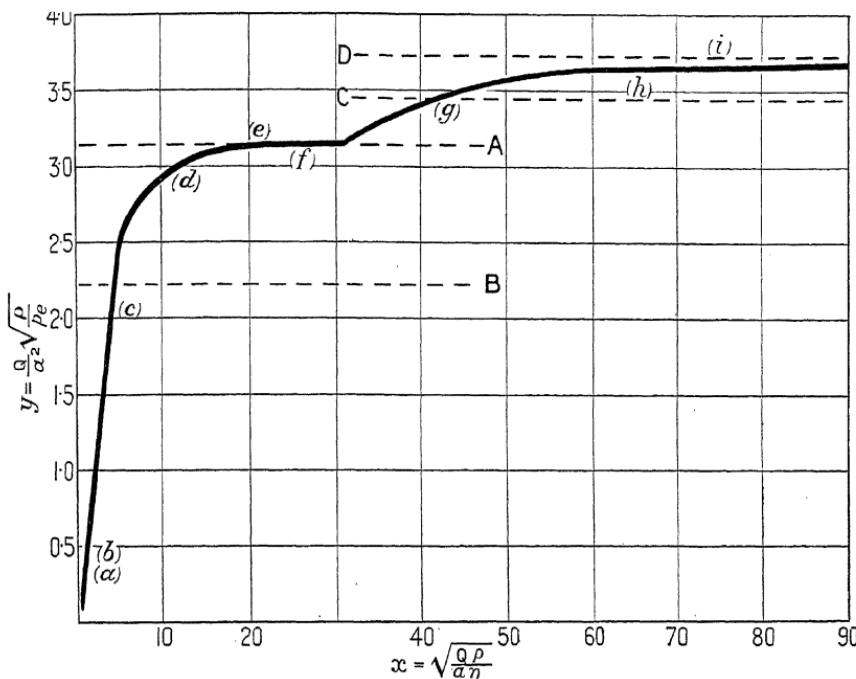
FIG. 2. Results of Bond's experiments on 'end effects' (after the figure in *Proceedings*

m term arises, not from any loss of head resulting from an imparting of kinetic energy to the liquid, but solely from the inertia of the liquid, from its tendency to preserve the direction of its velocity'. He prefers to speak of an 'inertia correction' rather than of a kinetic-energy correction, since kinetic energy is merely, in the case of submerged discharge, a temporary form of storage of energy, all the work done by the pressure being expended against viscous forces either in the capillary itself or in the reservoirs. He would apparently restrict the 'kinetic-energy correction' to the case considered by Hagenbach (see p. 15), where the discharge takes place into a gas and the energy is actually thrown away between the points at which the pressure is measured. Without

challenging this distinction, I have preferred to adhere to the usual practice of referring to the m-term as a kinetic-energy correction, even when the discharge is submerged.

In the calculation from which he deduces the theoretical value $m = 1$, Dorsey postulates that the flow occurs from a reservoir with a large free surface through a cylindrical capillary with sharp smooth edges and large normal faces into a second large reservoir, the radial extent of the faces of the capillary and the distances from the capillary to the walls of the reservoirs being so great that the flow is the same as if these were infinite. The conditions of Bond's experiments approximate to this ideal case and Dorsey deduces $m = 0.98$ from the part of the curve between $x = 4$ and $x = 33$ ($R = 10$ to 700), but recognizes three reasons for the variations found for m in actual viscometric practice. One is the configuration of the ends of the capillary, which are very frequently not sharp-edged: a second is the impedance offered to the development of the jet by the presence of the walls of the viscometer, an obstruction which increases the work done in the reservoir and thus apparently increases m. Thirdly, a tendency towards decrease of the kinetic energy delivered to the second reservoir would arise in tubes so short that the distribution of velocities over the cross-section was unable to become adjusted to that characteristic of long tubes.

The shorter of the pair of tubes used by Bond in obtaining the points (d) and (e) of Fig. 2 had a length only a little more than four times its diameter, while for the points (f) the length of the shorter tube was 13 diameters. Now the calculations of Boussinesq and of Schiller (see p. 19) indicate that the adjustment of the velocity distribution is not complete until the length of the tube is $0.03 R$ to $0.06 R$ times the diameter: a similar criterion has also been obtained experimentally by Schiller for pipes of circular cross-section and by Davies and White for rectangular pipes. At $R = 500$, corresponding with the highest velocity in series (f), it would therefore appear that a length equal to some 30 diameters should be required before the normal distribution of velocities over the cross-section of the tube was realized: the highest speed in series (d) requires a length of over 8 diameters. It is therefore probable that many of Bond's data in the range $R = 10$ to $R = 700$ are unsuitable for the deduction of the coefficient m for long tubes; at still higher velocities it is obvious that if turbulence occurs in

the longer tube and not in the shorter, the end-correction will not be the same in both. The dimensionless quantity against which the correction should be plotted is indicated by Schiller's reasoning to be Rd/l instead of R. This criticism does not, however, affect the validity of the deduction of $n = 1.146$ from the part of the diagram nearer to the origin.

(f) *The work of Schiller.* Schiller's experiments[29] were made by a method which, though unsuitable for routine determinations of viscosity in a physico-chemical laboratory, has proved invaluable to hydraulicians. The principle of the method consists in observing the pressure at certain points along a tube through which liquid flows at a measured rate from a large tank: the difference in pressure between two points represents, with certain limitations, the work done in the portion of the tube between those points. If the positions of the gauge points are so selected as to be beyond the influence of the ends, and the flow is so slow as to be laminar, it is obvious that we should have the conditions postulated in the analytical deduction of Poiseuille's Law for a tube of infinite length.

Experiments of this nature are particularly suitable for the study of the general laws of flow of fluids through pipes, and in order to facilitate comparisons between results obtained with different fluids in pipes of various diameters, it is usual, following a suggestion made by the late Lord Rayleigh, to plot the data obtained in dimensionless co-ordinates. If the 'resistance coefficient' λ be defined as equal to $\dfrac{p_1 - p_2}{l} \cdot \dfrac{d}{\frac{1}{2}\rho v}$ where p_1 and p_2 are the pressures observed at the beginning and at the end of the length l of tubing of diameter d, λ is a dimensionless quantity which may be plotted against $R = vd\rho/\eta$. In order to compress their observations into a convenient compass Stanton and Pannell[30] used log R as abscissa. Blasius[31] and more recent workers have plotted log λ against log R, a procedure which has the advantage of indicating Poiseuille's Law by a straight line inclined at 45° to the axes and of enabling the 'index law' for turbulent flow to be checked on the same diagram.

In order to obtain data from which to calculate the value of the kinetic-energy correction, Schiller attached one limb of a manometer to one of the gauge-points, far enough from the entrance that the velocity distribution could be demonstrated to be that

characteristic of an infinitely long tube, and connected the other limb to the tank from which the water was being supplied. The differences of pressure indicated by the manometer therefore included that due to the entrance conditions as well as that due to the unmodified flow in the tube: the distance of the gauge-point from the inlet was so great that any Couette correction would have been too small to affect the results. Measurements were made both with sharp-edged tubes of which the plane ends lay in the plane of the wall of the tank, and with tubes provided with a well-rounded bell-mouth presenting no discontinuity of profile. The observations of pressure difference and of the rate of discharge $Q = \frac{1}{4}\pi d^2 v$ of the water were reduced, by combination with the known length and diameter of the tube, to form dimensionless quantities suitable for the graphical derivation of m. Let equation (II. 7) be written, taking $n = 0$, as

$$P = \frac{8 Q \eta l}{\pi a^4} + \frac{m\rho Q^2}{\pi^2 a^4}$$

$$= \frac{32 \eta v l}{d^2} + m\rho v^2.$$

If both sides be divided by $\eta v l/d^2$, we obtain

$$\frac{Pd^2}{\eta v l} = 32 + m \frac{vd\rho}{\eta} \cdot \frac{d}{l}$$

$$= 32 + mR\frac{d}{l}.$$

When the quantity on the left of this equation is plotted against Rd/l a straight line should be obtained, the slope of which gives m.

Using a drawn brass tube of diameter 0·8 cm. and length 197·4 cm. or 104·7 cm., provided with a bell mouth which was estimated to increase the effective length by 0·6 cm., Schiller obtained plots giving values of m, varying in different series of tests from 1·06 to 1·23, the weighted mean of which is regarded as in good agreement with his theoretical value 1·08. With a narrower sharp-edged tube he obtained a similar result, $m = 1·19$, which held up to velocities only a little below those at which turbulence began; but when the bell mouth was removed from the 0·8 cm. diameter tube, the graph indicated a higher value of m, apparently varying with the velocity. He concluded that rounded entrances are essential for viscometric purposes (when the kinetic-energy correction is of importance).

In the above experiments the length of tube selected for test was never less than 130 diameters. By means of the theoretical treatment, of which the premises are stated on p. 19, Schiller was able to calculate the pressure-drops, corresponding with given rates of discharge, between the rounded entrance of a straight tube and a cross-section taken at any distance along the tube. He found that the drop could be expressed as equal to

$$\tfrac{1}{2}\rho v^2 \cdot f\left(\frac{x}{dR}\right),$$

where x is the distance of the section from the orifice; the value of $f\left(\dfrac{x}{dR}\right)$ for any value of the argument may be obtained from his equations by suitable interpolation methods. The pressure-drop between two gauge-points at different distances along the tube may then be found by subtraction. Measurements made with three tubes of diameters 0·8 cm., 1·6 cm., and 2·4 cm., on which the gauge-points were distant 1 and 2 metres approximately from the inlet, gave results in striking agreement with those predicted by the theory. The data plotted extend from values of $\dfrac{x}{dR}$ as low as 0·003 to values as high as 0·1; the Poiseuille distribution, it may be recalled (cf. p. 19), occurs for $\dfrac{x}{dR} > 0\cdot029$.

When the velocity is such as to make $\dfrac{x}{dR}$ for the former of the two gauge-points have a value less than 0·029, the axial filament of water in the tube between it and the second point is still under-going acceleration. Hence if, as in the previous series, the pressure-drop between the tank and the first gauge-point had been measured, the results for this 'leading-in' portion would have yielded a value of m less than 1·08. By suitable manipulation of the data obtained for the pressure difference between the two gauge-points it would be possible to find the values of m which must be assumed to hold for the flow in the leading-in tube. The calculation is not shown in Schiller's paper, but since his theory is so well confirmed, the variation of m may be deduced more simply from the curves expressing the theoretical variation of $f\left(\dfrac{x}{dR}\right)$. Schiller and Kirsten[32] give a curve, of the form shown in Fig. 3,

which was apparently obtained in this manner. It may be well to recall the fact that the theory underlying this formulation assumes that the tube is provided with a bell mouth, as was the case in the experiments by means of which the theory was verified. When the end of the tube is thus rounded it is inappropriate to apply a Couette correction to the length; but some estimate is desirable of the increase in the effective length of the tube if the widening is very gradual, e.g. Schiller added 6 mm. to allow for the effect of
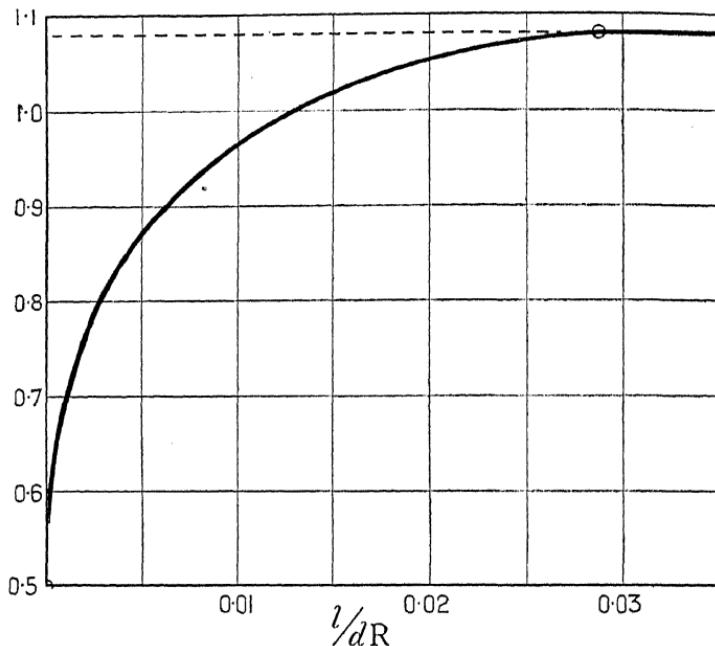
Fig. 3. Variation of m in short tubes (after Schiller and Kirsten).

a flare which extended to about 10 mm. before the diameter of 8 mm. was doubled.

(g) *Riemann's determination of* m. The most recent experimental determination of m is due to Riemann,[33] who used very fine capillaries (of diameters 0·0105 cm. and 0·0173 cm.) with their ends ground off at right angles to the axis. These capillaries were employed in a viscometer of the form recommended by Bingham for absolute measurements, so that the value of m obtained might be considered to be applicable to such an instrument. The necessary measurements were made with great care, using velocities so high as to make the kinetic energy equal to one-fifth to one-sixth

of the viscous work. The diameters of the tubes were calculated from the known viscosity of water, the experiments being made with water at temperatures from 22° C. to 36° C. Observations of rate of flow were made at about ten different pressures in each series and values of m were calculated for each of six series by Knibbs's method (p. 21): within the accuracy of the experiments the points obtained lay on straight lines giving $m = 1\cdot110$ to $1\cdot134$, mean $m = 1\cdot124 \pm 0\cdot006$. No Couette correction was applied, but since the ratio of length to diameter was 77 or 110, a correction with $n = 0\cdot573$ would make m only about $0\cdot003$ greater. Riemann recognizes that conical or elliptical tubes may give higher values of m and that the shape of the ends of the capillary and the dimensions of the exit reservoir may affect the result, but since his apparatus was fundamentally similar to the viscometers of Thorpe and Rodger and of Bingham, he advocates the use of Boussinesq's factor for similar instruments.

7. The transition from stream-line to turbulent flow. It has already been remarked that the simple relationships discovered by Poiseuille hold only for slow flow in relatively narrow tubes, and that the phenomena associated with flow on the scale more commonly observed in daily life are subject to more complicated laws. The full discussion of these laws lies outside the province of viscometry, but it is desirable that we should have some notion of the limits of speed and diameter at which Poiseuille's Law breaks down.

(a) *Hagen's temperatures of maximum discharge.* The first description of the transition from one régime to the other appears to have been given by Hagen,[34] who measured the rate of discharge of water from three pipes of diameter 3, 4 and 6 mm. at temperatures from 4° C. to 85° C.; the length of the smallest tube was about 0·5 metre, the other two being a little over a metre long; the pressures applied varied from 2 to 30 cm. On plotting the rates of discharge at constant pressure against the temperature of experiment, Hagen observed that the discharge increased to a maximum as the temperature was raised, then decreased and, after passing through a minimum, increased again less rapidly. The temperature of maximum discharge was found to be lower the greater the pressure and the wider the tube.

The part of the curve between the maximum and minimum

represents the stage of transition between two types of flow; Hagen noticed that these types were characterized by the appearance of the jet of liquid issuing into the air from the end of the tube. In both régimes the jet was steady, but at any temperature below that corresponding with maximum discharge from a given tube under a stated pressure the surface looked like polished glass, whereas at temperatures above that of minimum discharge the surface was wavy. Between the two 'critical' temperatures the jet was jerky and tended to oscillate between two extremes of length.

Brillouin (*Leçons*) describes a repetition of Hagen's experiment as a lecture demonstration: when water is allowed to flow through a horizontal glass tube 60 cm. in length and 0·28 cm. in diameter under a constant head of 20 cm., the maximum discharge occurs at ca. 22° C. and the minimum at ca. 40° C.; between these two temperatures the jet is inconstant. The transition from one régime to the other is more readily demonstrated by another experiment, also described by Brillouin, in which a column of mercury at room temperature was discharged through 35 cm. of a horizontal capillary tube of 1 mm. bore with trumpet-shaped inlet. When the head was more than 16 cm. the jet flowed steadily, but oscillations began when the head had fallen to 13·5 cm. and became violent between 12 and 7·4 cm.; with heads less than 7 cm. the jet once more flowed smoothly.

(b) *Reynolds's experiments*. The classical researches of Osborne Reynolds[35] must receive brief mention. He set out to investigate the circumstances which determine the type of flow of water. On the theoretical side he was faced with the fact that a general solution of the equations of motion of a viscous fluid was impossible. By assuming that the nature of the motion of water in a tube could be defined by the average velocity v and the diameter d of the tube, he showed that the ratio between the forces due to viscosity and those due to accelerations depended on the value of the quotient $vd\rho/\eta$. It will be noticed that the length was supposed to be without effect. The transition from one régime of flow to the other should therefore take place when this quotient has a certain definite value. A more general form of the result may be deduced by the method of dimensions (cf. Stanton and Pannell[36]), but the actual value of the criterion remains indeterminate. It is usual to

refer to the number obtained by evaluating $vd\rho/\eta$ as Reynolds's number or criterion (abbreviated R); since R is dimensionless its value is the same in any consistent set of units. Brillouin has shown that Hagen's experimental results afford some confirmation of the correctness of the supposition that the transition depends upon the value of R.

Reynolds proceeded to verify his conclusion and to obtain a definite value for the criterion of the relative stability of the régimes by two distinct series of experiments. In the first arrangement the nature of the flow through tubes, immersed in and discharging water from a large tank, was rendered visible by means of a coloured solution delivered from a nozzle near the mouth of the tube. The glass tubes were 5 ft. long and had diameters of $\frac{1}{4}$, $\frac{1}{2}$ and 1 inch: to each was fitted a bell mouth to steady the flow. The rate of discharge was controlled by a cock connected to the tube outside the tank. At low velocities the coloured water was drawn out into an unbroken filament which extended along the axis of the tube without appreciable spreading: any disturbance in the tank was reflected by a wavering of the filament. As the velocity was gradually increased, there came a time when the filament some distance from the mouthpiece suddenly spread out and coloured the whole cross-section of the tube; on closer examination this could be seen to be due to the formation of eddies. The distance from the entrance at which the eddies were first produced decreased as the velocity increased, but in no case was it less than 30 diameters. When the velocity was not much more than sufficient to produce instability, the eddies sometimes extended for only a few inches, were suppressed for the next few inches and reappeared further along the tube, giving the appearance of 'flashes' of colour. On lowering the velocity, the turbulent régime was replaced by stream-line flow.

These experiments, repeated at different temperatures from 4° C. to 22° C., sufficed to show that the value of R at which eddies appeared was approximately constant, but the measurements were not precise enough to fix the criterion very accurately. A second apparatus was therefore set up to observe the fall in pressure between two gauge-points 5 feet apart towards the discharge end of a lead pipe 5 to $5\frac{1}{2}$ yards long. The water was supplied from the mains at a regulated pressure; the rate of discharge at any moment, controlled by a cock at the exit end, could be deduced

from the height of the water-column in a recipient with an orifice
in the bottom, which had been calibrated as an orifice meter. The
pressure difference between the two gauge-points was read on a
differential manometer containing either carbon bisulphide or
mercury; the upper part of both limbs and also the connexions
from the manometer to the lead pipe were filled with water. Most
of the observations recorded relate to two pipes of $\frac{1}{4}$-inch and
$\frac{1}{2}$-inch diameter respectively. The results were expressed in terms
of the average velocity (= volume discharged per second divided
by area of cross-section) and the loss of head per unit length
between the gauge-points. When v was plotted directly against
$\frac{1}{\rho}\frac{dp}{dx}$, the points corresponding with the lower velocities lay on a
straight line passing through the origin, as required by Poiseuille's
Law; but above a certain point the results gave a curve convex to
the velocity axis. The velocity at which Poiseuille's Law ceased to
hold could be deduced from the intersection of the straight line
and the curve. Unmistakable evidence of some change in the type
of flow was also afforded during the course of the experiments, at
velocities close to this critical velocity, by the behaviour of the
manometer on which the readings of pressure-drop were taken.
At very high and at very low rates of discharge the readings were
quite steady, as was to be expected; but in the transition region
the carbon bisulphide or mercury showed violent and sudden oscil-
lations, so that only an average pressure could be recorded. It is
reasonable to correlate the occurrence of these oscillations with
the discontinuous production of eddies, or 'flashing', observed in
the previous series of experiments.

Since the loss of head in the turbulent régime was supposed,
from the results obtained by earlier hydraulicians, to be propor-
tional to some power of the velocity approaching the square,
Reynolds also plotted his data in logarithmic co-ordinates. On
such a diagram Poiseuille's law is represented by a straight line,
making an angle of 45° with the axes if the units are consistent;
if turbulent flow obeys an index law, the index may be deduced
from the slope of the 'logarithmic homologues' above the critical
velocity. From his own results and those of Darcy[37] Reynolds
deduced a law

$$\frac{dp}{dx} = kv^n, \qquad n = 1\cdot722. \quad . \quad . \quad . \quad \text{(II. 11)}$$

The pairs of straight lines corresponding with the experiments made with different tubes were all parallel and could be brought into coincidence by shifting them so as to make the points of intersection the same. Owing, presumably, to the inconstancy of the pressure readings near the critical point, or to the discontinuous production of eddies, the results near the intersection of the straight lines representing the two types of flow tended to lie above the extrapolation of the 'turbulence line'. The first definite departure from the straight line corresponding with Poiseuille's Law occurred, on the average, at a velocity such that

$$R = \frac{vd\rho}{\eta} = 2000, \quad . \quad . \quad . \quad . \quad \text{(II. 12)}$$

and the plotted points did not lie accurately on the turbulence line until the velocity corresponded with $R = 2400$.

The earlier experiments, using the coloured filament method, indicated a very much higher value for the criterion, viz.

$$R = 12800. \quad . \quad . \quad . \quad . \quad \text{(II. 13)}$$

The discrepancy is to be explained by the difference in the conditions of the observations. The upper limit (II. 13) is that at which stream-line motion was not possible for a distance greater than 30 diameters; the lower (II. 12) is that at which disturbances existing in the mains and connexions thereto were suppressed after the water had traversed some $3\frac{1}{2}$ yards of the pipe.

(c) *More recent work.* Later investigators (e.g. Stanton and Pannell[36]) have found little difficulty in confirming the substantial accuracy of Reynolds's estimate of the lower critical velocity. It has been shown that turbulent flow cannot persist in glass or metal tubes, even if the surface is fairly rough, below a velocity given by $R = $ ca. 2400. An extreme case of unevenness is mentioned by Schiller[38] who states that laminar flow was established at all velocities below $R = 2800$ in a brass tube of 1·6 cm. bore both before and after cutting a thread of 0·4 mm. pitch and 0·3 mm. depth on the interior; in this experiment the water from a tank traversed 52 cm. of the pipe (with sharp-edged entrance) before reaching the section over which pressure measurements were taken.

For the higher critical velocity very different values have been put forward from time to time. Reynolds himself laid stress on the fact that the slightest disturbance of the water in the tank from which the water was discharged in his coloured-filament

experiments led to the production of eddies at considerably lower velocities than corresponded with $R = 12800$. By using very large tanks, by waiting for a long time for the water of the tank to come to rest before starting the flow, by improving the construction of the bell mouth, &c., other observers have been able to obtain laminar flow at very much higher velocities. Barnes and Coker[39] observed that no turbulence occurred, in a pipe 1·5 metres long and 5·4 cm. in diameter, even at $R = 50,000$; but they could not obtain such high values with pipes of smaller bore and of similar length. These authors used a thermal method to detect the break-down of laminar flow; they found that if the walls of a pipe were slightly warmed, the beginning of turbulence was signalized by a sudden change in the temperature indicated by a thermometer placed axially in the tube down-stream. Camichel[40] drew attention to the effect of the length of the tube on the value of the criterion and Schiller[41] has examined in considerable detail the effect both of initial disturbances and of length of the lead-in tube. Since the available evidence appears to indicate that the upper critical velocity is independent of the roughness of the walls, at any rate for technically smooth tubes, and is merely a function of the freedom from disturbance in the tank or of the perfection of the bell mouth, Schiller recommends that the conception of an upper limit be no longer retained. He prefers to speak of '*the* critical number' as the lower limit below which it is impossible for turbulent flow to persist in a long tube however much initial disturbance there may be: for this criterion his experiments give $R = 2320$. By gradually reducing the violence of the initial disturbance, as by increasing the distance of a plate in the tank from the bell mouth of the tube, he was able to preserve the condition of stream-line flow, which tends to occur near the convergent entrance, at higher and higher velocities; but above $R = 2320$ the laminar régime is metastable and requires progressively smaller disturbance to cause its breakdown.

If observations are made on a sharp-edged pipe near its junction with a wider vessel, the lower limit may appear to be raised slightly, but in these circumstances the transition between the two régimes is not abrupt. The data obtained in such experiments are best plotted in the manner suggested by Blasius (see p. 31). Schiller gives a number of log λ — log R diagrams showing the results of his measurements, and his conclusions may be illustrated

by Figs. 4 A and B. The abrupt change of régime shown in Fig. 4 A occurs only when the length of the leading-in tube is sufficient to damp the effect of perturbations at the entrance. When the leading-in tube is short the points obtained for the laminar régime deviate from the Poiseuille straight line at moderately high values of R, owing to the fact that the velocity distribution has not become parabolic before the first gauge-point is reached. Curves I and II, in each figure, show the type of result obtained when the disturbance at the entrance is negligible (bell-mouthed tube in quiet tank) and considerable (sharp-edged tube with unsteady supply).

In later experiments Schiller[42] showed that when the disturbance
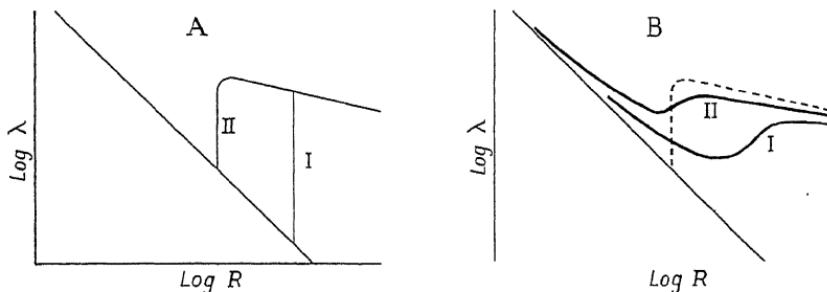
FIG. 4. Effect of entrant length on transition to turbulent flow (after Schiller). Lead-in: A. long; B. short. Disturbance: I. negligible; II. considerable.

at the entrance to the tube was very small the velocity at which laminar flow appeared to break down depended in a marked degree on the length of the leading-in tube before the first gauge-point. The transition began to take place at $R = 20,000$ for $x = 80\,d$ but the critical value fell steadily to $2,320 - 2,800$ for $x = 400\,d$: no further drop could be recognized when the leading-in tube was lengthened to 1,300 diameters.

Some confirmation of this effect of the length of leading-in tube appears to be afforded by the recent work of Davies and White[43] on flow between flat plates. These authors found that deviations from the theoretical discharge for stream-line flow first occurred at $\dfrac{vd\rho}{\eta} = 890$ (d is now the distance between the plates) for all entrant lengths greater than $\dfrac{x}{d} = 54$, but as the gauge-points became relatively nearer to the entrance the deviations were noticeable at lower velocities. Extrapolation of their curve indicated

that for $x/d = 0$ the critical number would be $vd\rho/\eta = 140$, i.e. that eddies could not exist anywhere in a rectangular pipe at velocities lower than correspond with this number, whatever might be the conditions before the entrance. It should be noted, however, that this interpretation of the curves of Davies and White ignores the effect of kinetic-energy corrections or deviations from parabolic velocity distribution and that the transition from viscous to turbulent flow was shown by all their curves to be very gradual.

For obvious reasons most of the investigations regarding critical velocity have been made on water not far from room temperature, so that the establishment of a definite Reynolds's number has involved merely an inverse variation of mean velocity with diameter. Large tanks of hot water show marked convection currents which hinder the preservation of stream-lines at high rates of discharge through pipes connected with them, so that experiments on 'upper limits' become impractical, as Reynolds himself found. But Coker and Clement[44] were able to show that the 'lower' critical velocity was proportional to the viscosity over a range of temperature from $4°$ C. to $50°$ C. Coker [45] also demonstrated that the reciprocal relation between critical velocity and the diameter of the tube held for the flow of mercury. Grindley and Gibson[46] and Ruckes[47] have studied the transition in the flow of compressed air.

(d) *Application to viscometry.* The inference to be drawn from these and other experiments is that, at velocities below $R = 2,320$, turbulence cannot persist throughout a cylindrical tube even though there may be much disturbance in the reservoir from which the liquid is being delivered, provided the tube is some 130 diameters long. Since the condition of turbulent flow is unsuitable for the determination of viscosity, the resistance offered by the tube being more nearly proportional to the density than to the viscosity of the liquid, precautions are normally taken to ensure that the flow shall be laminar; unsymmetrical projections near the mouth, for example, and intentional stirring of the liquid are avoided. The most serious disturbance is likely to be found at the junction of the reservoir and the tube. If the junction is well-rounded and the tube is short, stream-line flow may persist at velocities as high as those corresponding with $R = 30,000$ to $50,000$, but when the entry to the tube is quite sharp, transition to turbulent flow may occur down-stream at $R = 2,320$ if the tube is long enough. In

short tubes the transition is indefinite but appears to take place at velocities uniformly higher than $R = 2{,}320$, even when the edge is as sharp as possible. Thus, Erk[48] observed a critical Reynolds's number $R = $ ca. 3,500 for flow through the sharp-edged outlet tube of an Engler viscometer. Stream-line flow tends to persist when the axial filaments are being uniformly accelerated, either in the establishment of parabolic distribution or owing to convergence of the tube.

In experiments with high rates of discharge, such as are frequently made in attempting to derive an accurate estimate of the coefficient m of the kinetic-energy term, the plotted data are likely to make m appear to be smaller than 1·12 at the highest velocities, if these are such as to make l/dR as low as 0·03. On the other hand, a discontinuous production of eddies by sharp edges at the entrance or by small irregularities will occasion increased resistance, which may be interpreted as due to a gradual transition towards the turbulent régime, but will make m, as deduced from a Knibbs's diagram (see p. 21), appear to increase at the higher velocities, even below $R = 2{,}320$. It may be well to emphasize the fact that the conditions prevailing in viscometers as the rate of flow is increased, either by increasing the applied pressure or by decreasing the viscosity, are not such as tend to make the breakdown of Poiseuille's Law be indicated in such diagrams as those of Knibbs and of Herschel (see p. 24) by any abrupt change in slope. The first production of eddies will occur, in 'flashes', towards the exit end, so that the increase in resistance will be small: at higher velocities the 'flashes' will gradually become more numerous and arise nearer to the entrance; but at no stage will there be a sudden transition from laminar to turbulent flow throughout the tube. Where the head is varying during an experiment, as in tests on technical tube viscometers, the transition is further concealed by the fact that eddying motion may occur at the beginning of a run and give way to stream-line motion as the head is reduced.

8. Slipping. This chapter would be incomplete without a reference to the effect of possible 'slipping' due to imperfect adhesion between the liquid and the walls of the tube. The literature of the subject however, has been fully reviewed by Bingham (*Fluidity and Plasticity*) so that it is unnecessary to discuss it again here. It will suffice to recall the equation deduced by Helmholtz, who

showed that if slipping occurred at the wall of a tube the Poiseuille equation (II. 3) would need to be modified by the substitution of a^4 by

$$(a^4 + 4\frac{\eta}{\beta}a^3) \text{ or } (a^4 + 4\epsilon a^3).$$

Here β denotes the coefficient of sliding friction between the liquid and the wall ('external friction' in German writings) and ϵ is a quantity which represents the distance outside the liquid-solid surface at which the velocity would become zero if the velocity-gradient were supposed to vary at and beyond the wall at the same rate as inside the tube. The verification of Poiseuille's Law of diameters in experiments made both with water and with mercury over a wide range has provided the most convincing proof of the incorrectness of some earlier observations, which appeared to warrant the assumption of a measurable sliding friction for normal liquids in contact with solids. The error has been traced in some cases to inaccurate measurement, in others to incomplete theoretical treatment. The absence of slip at the wall has been taken for granted by most workers since the date (1908) of Ladenburg's repetition of an oscillating-sphere experiment due to Piotrowski, on which Helmholtz had based a high estimate for ϵ. Quite recently, however, claims to have established the existence of slipping have been made in two quarters:

1. Tammann and Hinnüber[49] measured the viscosity of mercury with the aid of metal capillaries. In steel and nickel tubes they found values not very different from those recorded by other observers who had used glass tubes; but with amalgamated copper tubes they obtained readings indicating a viscosity about three times as high. In a crucial experiment they noted that the rate of flow of mercury through a chemically cleaned copper tube decreased for several days before reaching a fairly steady value; on examination of the tube, the thickness of the amalgam layer was found to be quite insufficient to allow the retardation to be explained by the reduction in cross-section of the tube. They therefore suggested that older determinations in glass tubes were vitiated by the occurrence of slip at the walls. In a critical review of the earlier data Erk[50] showed that the concordance between results obtained by different methods and with tubes of different diameter was sufficient to exclude the possibility of significant errors due to this cause; he suggested that the effective thickness

of the layer of amalgam might be considerably greater than would be found by the method of estimation adopted by Tammann and Hinnüber. The results cannot be explained by an increase in viscosity due to the dissolution of copper in the mercury, since the solubility is so small as to occasion a maximum increase of only 0·3 per cent. Bingham and Thomson[51] appear to have discovered the true reason for the discrepancy in the observation that a smooth surface of copper becomes visibly rough in a few hours after amalgamation: large crystals grow, in the saturated amalgam, at the expense of the smaller crystals and may protrude as much as 0·5 mm. from the surface after two weeks of growth. Such recrystallization would occasion no alteration in the average diameter of a capillary but would very seriously decrease the effective diameter: Bingham and Thomson found that flow through a small amalgamated capillary ceased altogether after a time.

2. Traube and Whang[52] made experiments on the effect of coating the walls of the capillary with layers of different small thicknesses of a number of organic compounds, and found that the time of flow of a given volume of water through the capillary was in some cases very materially reduced. The effect was very pronounced with oleic acid, applied by running an ethereal solution (1 to 10 per cent.) through the tube, draining and drying; other substances more soluble in water showed a similar behaviour, but in general the effect was marked only with polar, surface-active compounds and was small or absent with non-polar compounds such as paraffins. These authors concluded that the results obtained were due to slipping at the interface, and their theory was developed in some detail by Weber and Neugebauer[53] with reference to the work of Langmuir and others on the orientation of molecules in surface films. While it is impossible, without further experimental evidence, to deny the possibility of the existence of slip in some of the cases reported by Traube and Whang, exception may be taken to the viscometry on which their claims are based. The instrument used was one devised by Traube and Magasanik[54] which consists of a capillary inclined at a small angle to the horizontal, the discharge end being bent so as to be nearly vertical, and the fiducial volume marks being placed towards the upper end of the inclined part of the capillary. The effective pressure producing flow is thus the hydrostatic head *minus* the head due to surface tension; the hydrostatic head is

small, so that surface tension has a relatively large influence, and Traube and Whang found, in fact, that the effects of the surface films were reduced if the flow was accelerated by an increase of pressure and became negligible in viscometers of more conventional form. It is reasonable to assume that the increases in rate of flow which they observed for tubes coated with films of polar substances were due to lowering of the surface tension of the water by the dissolution of some of the film and the concentration of this impurity in the water-air meniscus. A determination of the viscosity of glycerol in one of these instruments, mentioned by Traube and Magasanik, appears to provide sufficient evidence to render this criticism justified, for the value found was absolutely inconsistent with accepted data. A similar criticism has quite recently been offered by Tausz and Körösy[55] who have worked out an equation for the calculation of viscosity from observations made with such apparatus, and have demonstrated the effect of a reduction of surface tension at the meniscus.

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TUBE VISCOMETERS FOR ABSOLUTE MEASUREMENTS

IT will be readily appreciated from a perusal of the chapter which now follows that the accurate determination of the coefficient of viscosity of a liquid, by the capillary tube method, in terms of the fundamental units of length, mass and time is a problem calculated to tax the resources of the best equipped physical laboratories. Difficulties of a similar magnitude arise in other measurements, e.g. in the practical realization of the thermodynamic scale of temperature. In the example cited, these difficulties do not prohibit accurate thermometry by workers outside such laboratories who are content to let their determinations of temperature be not absolute but relative to the fixed points defined by competent authorities. In practical viscometry it is rarely necessary for the investigator to undertake the labour involved in the evaluation of the constants of his instrument *ab initio*: he may, as in the case of thermometry, rely on standards set up by others. This procedure not only avoids the probability of errors due to the use of inadequate apparatus and technique but allows the use of viscometers of a form more suitable for routine measurements. The description of such viscometers and of the methods by which they may be calibrated forms the subject of Chapter V: in the present chapter we shall deal with absolute as distinct from relative viscometry, although some of the details here included may be of use in both connexions.

1. Development of the absolute viscometer.

(a) *Defects of Poiseuille's apparatus: Early improvements.* The apparatus used by Poiseuille (p. 11) suffered from the following defects when used for purposes beyond those for which it was designed:

(i) The liquid under investigation was discharged into the thermostat: this was objectionable when valuable or corrosive liquids were in use and necessitated refilling and readjustment of the viscometer for every repetition of an experiment.

(ii) It was not possible to measure the length of the capillary after it had been sealed in position, and it was only by the destruction of the apparatus that it was possible to be sure that the bore

had not been distorted at the junction of the capillary with the wider tube.

(iii) The bulb in which the volume of efflux was measured was of a shape such that differences in rate of drainage might cause errors of delivery either when different rates of flow were secured for the same liquid by the use of different pressures or when liquids of different viscosity or surface tension were compared at similar rates of flow.

(iv) Solid impurities which might accidentally be suspended in
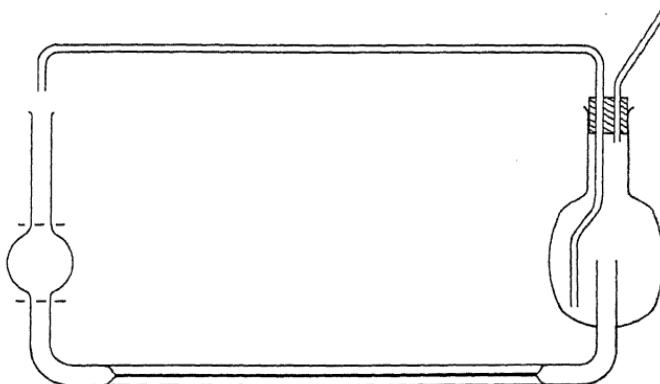
FIG. 5. Slotte's viscometer.

the liquid were almost certain to find their way into the capillary during the discharge.

In the viscometers described by subsequent workers the above-mentioned defects have been recognized and attempts have been made to eliminate them. Sprung[1] and Slotte[2] introduced slight modifications into the arrangement used by Wiedemann.[3] They avoided waste of liquid and pollution of the water-bath, without sacrificing the simplification of theory due to the maintenance of a constant pressure at the discharge end of the capillary, by sealing to the exit a wider tube which was bent upwards and cut off in the plane of the middle of the bulb: the liquid which overflowed from this orifice was caught in a receptacle attached by a cork, or sealed to the upturned tube, and was returned to the bulb, when a redetermination was required, by a siphon or 'wash-bottle' arrangement. Sprung also provided a dust trap, by allowing the entrance end of the horizontal capillary to project into a wider vertical tube below the bulb, so that solid particles might settle

out below the entrance: he was not, however, convinced of the utility of this precaution, and the trap was omitted by Slotte, a diagram of whose apparatus is shown in Fig. 5.

An obvious method of conserving the experimental liquid is to attach a reservoir to the exit end of the capillary. This procedure involves, of course, an increase in hydrostatic pressure at this point during the discharge, and the variation of head during an experiment necessitates the application of a correction which may become important if the head producing flow is small. In deter-
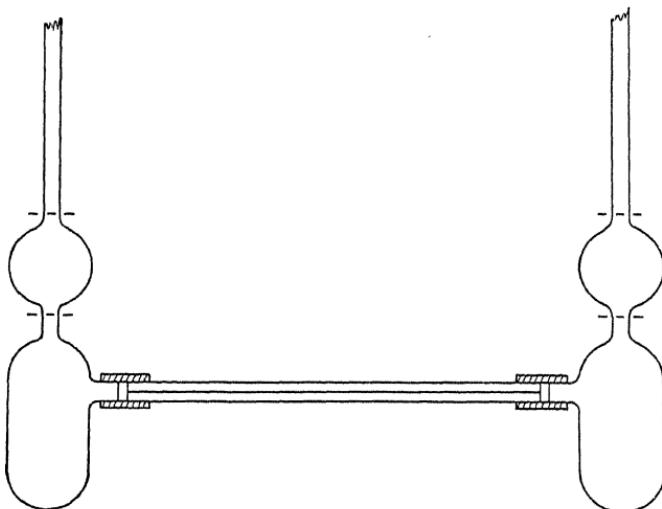
FIG. 6. Brückner's viscometer.

mining the viscosity of mercury, Warburg[4] avoided the need for such a correction by a somewhat troublesome manipulation; Koch[5] allowed the mercury to discharge into a vertical tube of approximately the same bore as the cylindrical bulb and worked out the logarithmic formula for the mean head which is given in § 2 B (3) b. In dealing with liquids other than mercury it is not difficult to ensure that the mean head shall be approximately equal to half the sum of the initial and final heads, and the necessary conditions have been realized in most absolute determinations.

Variations of the hydrostatic head at the ends of the capillary during the flow of a given volume of liquid may of course be minimized by increasing the diameter, not only of the measuring bulb but also of the recipient. If the liquid used is one that wets the glass, undue vertical shortening of the measuring bulb would lead

to drainage errors if the tubing above and below the bulb were constricted with the object of increasing the accuracy in the measurement of volume: actually, no worker has used a bulb shorter than its diameter, so far as I know. If the recipient bulb has the same volume and form and is at the same height as the measuring bulb, and the quantity of liquid in the viscometer is such that one bulb is just empty when the other is just full, the mean hydrostatic head becomes approximately zero: for the small correction that remains see §2 B(3)b. A viscometer embodying this feature was used by Brückner[6]: his apparatus (Fig. 6) included dust-traps at each end of the capillary, connexions being made by rubber tubing.

(b) *Viscometers of Thorpe and Rodger and of Bingham.* A number of improvements were introduced by Thorpe and Rodger[7] whose viscometer is illustrated in Fig. 7. The two vertical arms were made as nearly similar as possible; errors due to drainage were minimized (a) by using a cylindrical measuring bulb so that most of the wetted area was vertical, (b) by allowing the flow to start when the liquid was in a bulb of the same diameter above the constriction, so that the rate of drainage should be approximately the same when the meniscus was passing the upper and lower fiducial marks. The weight of water left on the walls of a similar bulb

FIG. 7. Thorpe and Rodger's viscometer.

after discharge through a capillary was found to be less than 0·1 per cent. of the content. Since measurements were to be made on each liquid at several different temperatures, it was necessary to adjust the total working volume afresh at each temperature if a constant mean hydrostatic head was to be assumed. In order to render the adjustment as precise as possible, while avoiding disconnexion of the tubes leading from the viscometer to the

compressed air reservoir, an 'inverted pipette' method was used; the working volume was defined by forcing the liquid down in the right-hand limb to the mark k_2, while a slight excess overflowed at H_1 into the trap there provided. This adjustment was repeated before each determination of the rate of flow at successively higher temperatures. The volumes above m_1 and above m_3 served to allow the operator time to get ready to start the stop-watch after applying the pressure. A duplicate determination was made at each temperature, after the liquid had been blown from the left to the right bulb, by adjusting to the mark k_1, with overflow at H_2, and then reversing the application of pressure and timing from mark m_3 to m_4; to allow for the possibility of slight evaporation between retests, the working volume from k_1 to H_2 was very slightly less than that from k_2 to H_1.

Nearly all of the liquids with which Thorpe and Rodger were concerned were organic, and would have acted to some extent on rubber. In order to be able to use a capillary of accurately measured length without resorting to rubber connexions, they joined the two vertical limbs by a cross-piece of thin-walled glass tubing, of which the bore was about 1 mm. greater than the external diameter of the capillary, and sealed the latter into the middle of this tube. The plane ends of the capillary thus projected into dust-traps at the bottom of the two vertical limbs. The method of sealing is liable, however, to introduce some uncertainty into the estimated effective bore: in guarding against distortion of the capillary the junction tends to become somewhat fragile. Further, the narrow annular spaces between the inner and outer tubes are difficult to clean and dry. These disadvantages have prevented other investigators from adopting this method of attachment of the capillary. Thus, Hosking[8] reverted to the use of rubber, the capillary projecting through a tubulure into a large spherical dust-trap: the junction was made tight by rubber bands. Since his experiments were made on water, these bands were not objectionable; he was also able to use an automatic electrical method of timing: the passage of the meniscus was indicated by the breaking of circuits between two pairs of platinum wires sealed into the narrow tubing above and below the bulb; the time of flow of the volume defined by the position of these contacts was recorded on a chronograph.

A simple modification of the Thorpe and Rodger instrument was

effected by Bingham and White[9] which avoids both the use of flexible connexions and the danger of distortion of the capillary. This consists in making a ground-glass joint between the capillary and the dust-trap. The device allows the capillary to have plane parallel ends so that the length as well as the diameter may be re-examined at any time: if a standard taper is adopted, other capillaries may be substituted in the apparatus. The ground joints may be held together either by the use of metal clamps or by stretching pieces of rubber tubing tightly over them.

In Bingham's latest form of absolute viscometer the overall length of the limbs is reduced by shortening the bulbs; instead of being cylindrical or spherical the bulbs are designed to assume approximately the form of two funnels placed base to base; the natural rounding of corners leads to the shape shown in Fig. 8. The tubing just above each bulb is similarly funnel-shaped with the object of making the drainage conditions as nearly as possible the same when the meniscus is passing the upper and lower marks of the measuring bulb. It will be observed that one of the two overflow points of Thorpe and Rodger's instrument has been discarded. This simplification necessitates the addition of fresh liquid, when any evaporation has occurred, before a second flow-time

FIG 8. Bingham's viscometer (after Bingham, *Fluidity and Plasticity*).

can be determined. A check on the absence of any appreciable evaporation, or of leakage at the ground joints, is valuable, however, and may be made by noticing whether any change has occurred in the working volume defined by the mark 1 and the 'pipette' opening at F. The volume of the reservoir bulb V^1 on the right-hand limb is made as nearly as possible the same as that between marks 2 and 3 in order that the hydrostatic-head correction may be small, but no graduations are required here since the rate of flow from right to left is found by observing the time required to *fill* the left-hand or measuring bulb.

Suppose now that the ratio between the times of emptying and of filling the measuring bulb, when the same pressure is applied to the left- and right-hand limbs respectively, is known for water; then if, in experiments with a more viscous liquid, a different ratio is obtained inconsistent with the magnitude of the change in the hydrostatic-head correction due to the change in density of the liquid, a clear indication is given of the existence of drainage errors. In the construction of the viscometer special attention is paid to ensuring (a) that the bulb V^1 shall be of nearly the same volume and shape as V and shall have its centre at the same height above the horizontal capillary, and (b) that the small bulb C^1 below V^1 shall have the same volume as is comprised between the mark 3 and the overflow orifice at F. If these conditions were realized exactly, the rising and falling menisci would be in tubing of the same diameter at any given moment during a determination, thus eliminating error due to surface-tension. The effects of drainage and of surface tension will be discussed later (see § 2 B (3) a and § 2 C (3)). The two other small bulbs, below V and above V^1, are also approximately equal in volume to that above V.

(c) *Stone's viscometer.* If the horizontal capillary of a viscometer is long, the instrument becomes somewhat fragile and of an awkward shape, and accurate levelling is necessary in order to make the hydrostatic head reproducible. A 15 cm. vertical capillary with ground joints was used by Stone[10] for absolute measurements on oils. The viscometer had the form illustrated in Fig. 9, from which it will be seen that the use of bulbs with constrictions was avoided by providing platinum points on the axis of a cylinder, the measured volume being defined by the rise of the meniscus past these points. The ground joints were held together by three brass tension rods and the compactness of the apparatus allowed a small bath to be used so that measurements at different temperatures could be obtained rapidly. The adoption of a cylindrical form for the measurement of volume enables the hydrostatic-head correc-

FIG. 9.
Stone's viscometer (after the figure in *Engineering*).

tion to be calculated with accuracy, and minimizes drainage and surface-tension effects, but these advantages are obtained at the cost of some sacrifice in the precision with which the volume can be determined. There is no apparent reason why a vertical capil-
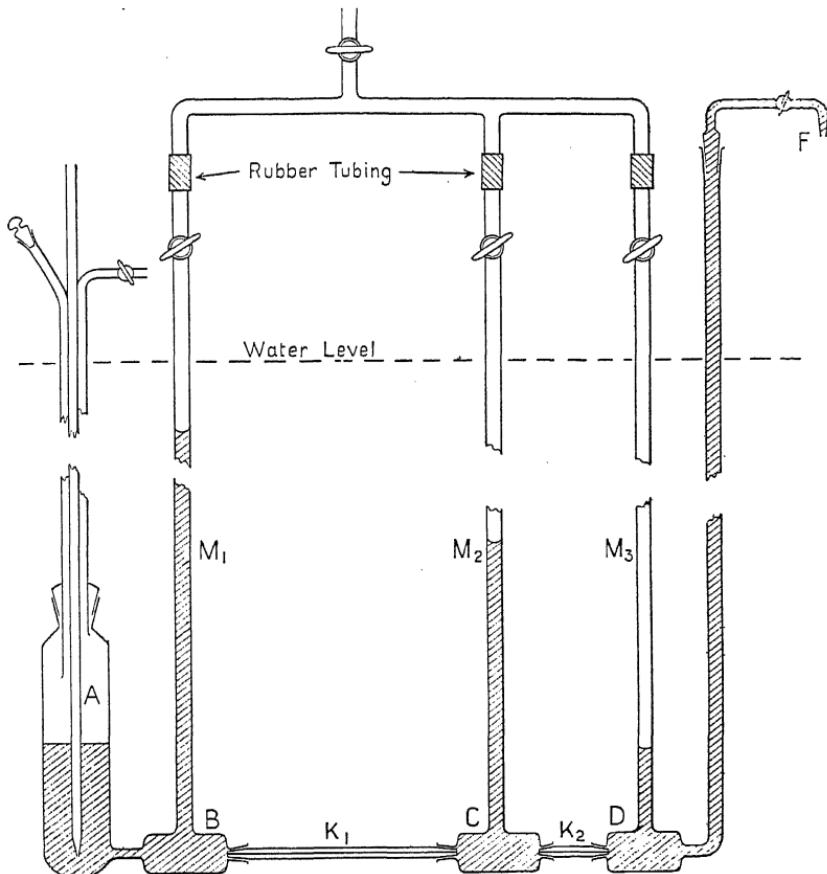
Fig. 10. Erk's viscometer (diagrammatic).

lary should not be used with an arrangement of bulbs and overflow device such as is employed in Bingham's form; slight drawbacks would be the absence of efficient dust-traps and the necessity for the provision of a fresh limb on the recipient side when the length of the capillary is varied.

(d) *Erk's viscometer.* A radical departure from the above types of viscometer has been made by Erk in recent work at the Physikalisch-technische Reichsanstalt, Berlin-Charlottenburg. Erk's

apparatus[11] is essentially a development of that of Couette[12] in which corrections to Poiseuille's Law due to the finite length of the tube are eliminated by the use of two capillaries of different lengths in series. Apart from the duplication of capillaries, the method resembles that used in hydraulic experiments, a steady rate of flow through the tube being established and measured by collection of the effluent liquid, while the pressure difference between the two ends of the capillary is read directly as a difference of head. A diagram of the apparatus is shown in Fig. 10: liquid is forced from the Mariotte bottle A by compressed air, of constant pressure, through the two capillaries K_1 and K_2, and is collected and weighed in a recipient placed below the outlet F for a suitable time. The capillaries are ground into wide tubes B, C, D, from which rise manometric tubes, M_1, M_2, M_3; from the heights of the liquid columns in these vertical tubes the loss of head due to each capillary is obtained. The whole system is immersed in a deep thermostat to a level indicated by the dotted line, and in order to bring the menisci in the manometric tubes below the level of the bath liquid a suitable common pressure of air is applied to the upper ends of these tubes. As a matter of convenience, the tube C is of such a shape as to make K_2 lie behind and parallel to K_1 instead of along a prolongation of the axis as in the diagram. The maximum pressure difference between the ends of the capillaries is limited by the vertical height of the tank, so that it is necessary to use different pairs of capillaries for different ranges of viscosity.

Since the two capillaries, even when cut from the same piece of tubing, are not likely to be of identical bore, Couette's equation (II. 10) requires slight modification. Owing, apparently, to leakage of air from the rubber tubing attached to the top of the manometric tubes, Erk found that the menisci in these tubes all rose slightly during the course of an experiment; hence the volumes flowing through the two capillaries were not exactly equal to one another, and a further small correction was necessary. For small differences between the radii a_1 and a_2 and between the volumes V_1 and V_2 the viscosity is given by the equation,

$$\eta = \frac{t}{8\pi} \cdot \frac{p_1 a_1^4 - p_2 a_2^4}{V_1 l_1 - V_2 l_2}, \quad . \quad . \quad . \quad \text{(III. 1)}$$

where the suffixes 1 and 2 refer to the longer and shorter capillaries respectively and p_1 and p_2 are the pressure differences between the

ends. The conversion of the measured heads into pressures and of the weight of effluent into volume requires, of course, a knowledge of the density of the liquid at the temperature of the bath.

The necessity or advisability of adopting Couette's method for the elimination of the kinetic-energy correction and of the Couette correction in absolute viscometry is somewhat doubtful. In the first place the principle of the method depends on the assumption that each of the capillaries is so long that in a certain part of its length the flow is exactly that which would occur in an infinitely long tube of the same cross-section. Erk used one tube having a length less than 50 times its diameter and took it for granted that this length was sufficient to make the foregoing assumption justifiable. According to the criteria calculated by Boussinesq and by Schiller (equations II. 5 and II. 6) this would seem to be the case in experiments made with oils such as were examined by Erk, but the criteria do not profess to be derived from a rigid analysis. Secondly, it is assumed that the ends of the capillaries and the conditions of flow in the wider tubes to and from which they lead are exactly similar: the presence of microscopically small chips in the ground sections and the reversal of the direction of flow at C may conceivably produce appreciable differences. It would appear to be safest (cf. Chap. II, § 6 (e) and (f)) to select even for the shorter tube one so long in proportion to its diameter that variations of m and n from those commonly assumed can produce only negligibly small errors: but when this has been done there is little point in adopting the Couette arrangement.

On the other hand, the maintenance of a constant rate of flow, for a time limited only by the capacity of the Mariotte bottle, and the measurement of volume by collection of the effluent liquid, offer certain important advantages. The troublesome correction for the variation in hydrostatic head in more conventional viscometers is obviated by Erk's arrangement; further, a redetermination of the rate of flow under a given head necessitates only the substitution of a fresh receiver at F, so long as the contents of A are not exhausted. Since the volume discharged is not measured by the emptying of a bulb, no errors due to surface tension or to incomplete drainage occur. The occurrence of slight errors in starting and stopping the collection of the liquid discharged necessitates the use of larger volumes than suffice for viscometers such as that of Thorpe and Rodger. If volatile liquids are to be

examined, precautions will need to be taken to guard against evaporation. These objections are, however, of little weight since it is possible to select, for absolute measurement of viscosity, liquids of which there is no stint and which are relatively unaffected by exposure to air, reserving scarce or volatile liquids for comparison with these in viscometers of suitable design adapted for relative determinations.

2. Design and calibration of viscometers of the Thorpe and Rodger type.

(*A*) *The capillary tube.*

(1) The dimensions desired.

In view of our uncertainty as to the precise values which should be given to the coefficients m and n of the amended Poiseuille equation when it is applied to the flow of a liquid through a viscometer, it is necessary either to determine experimentally the values appropriate to the construction adopted or else to select dimensions such that the uncertainty introduces a negligible error. Knibbs's graphical method for the evaluation of m has been explained in Chapter II § 6 (a); from examples quoted in the literature it appears to be possible to obtain an accuracy of 0·5 per cent. or so in this determination under favourable conditions. In the descriptions which have appeared, however, no proof has been afforded that the value deduced from the rate of flow of water under different applied pressures was not affected by some error due either to incomplete drainage of the bulb at the higher rates or to effects of surface tension or of hydrostatic head in the viscometer at lower velocities. The methods for the estimation of n which have been discussed in Chapter II § 6 (c) (d) involve either the destruction of the capillary, together with an assumption, in the method used by Bingham and White, that the conditions at the inlet are exactly reproduced at the broken portions, or else an accurate knowledge of the viscosities of a number of calibrating liquids. Hence it becomes necessary, in this connexion, to rely to some extent upon the experience of others and to use a capillary so long that the error due to the omission, or to the adoption of a possibly inaccurate mean value, of the Couette correction will be negligibly small. From the considerations advanced in Chapter II § 6 (e) there is some probability that the Couette correction for a sharp-edged capillary may vary, at different Reynolds's numbers,

between about $1 \cdot 15a$ and $0 \cdot 57a$. It is obvious that no error in viscosity determination as great as $0 \cdot 1$ per cent. should arise from such a variation if the length of the capillary is at least 300 times its radius and a value of $0 \cdot 9$ is assumed for n. Bingham suggests that the length be not less than 500 radii and assumes $n = 0$; this gives a possible error of the same order.

Let us suppose that it is desired to assume a value $m = 1 \cdot 12$ (or $m = 1 \cdot 10$, as the mean of Boussinesq's and Schiller's estimates) for the coefficient of the kinetic-energy term, and to design the viscometer so that no error as great as $0 \cdot 1$ per cent. will be produced in the estimation of viscosity if there is a variation of 10 per cent. from this value; such a variation is greater than has been reported for the majority of sharp-edged tubes used in careful determinations. The maximum radius to be specified for the capillary may then be derived as follows:

The assumption is that one-tenth of the second term on the right of equation (II. 7) shall be less than $0 \cdot 1$ per cent. of the first; this may be written

$$\frac{m \rho Q^2}{\pi^2 a^4 P} < 0 \cdot 01,$$

or, more generally, after substituting an approximate value for Q,

$$\frac{m \rho a^4 P}{64 \eta^2 l^2} < \epsilon.$$

Hence

$$a^4 < 64 \frac{\eta^2 l^2 \epsilon}{m \rho P}. \quad . \quad . \quad . \quad . \quad \text{(III. 2)}$$

Now convenience will usually fix an upper limit for l, and the means available for measurement of pressure, together with a desire to avoid errors due to surface tension and to hydrostatic head in the viscometer, will indicate a lower limit below which P is not to be reduced. Bingham suggests $l < 20$ cm., and $P > 50$ cm. of water. If we adopt these limits, equation (III. 2) shows that the maximum radius for the capillary will depend on the square root of the viscosity.

The viscosities of liquids boiling at atmospheric pressure have been found to be almost always greater than $0 \cdot 2$ cp. If our viscometer is to be suitable for the least viscous liquids we thus have, taking $m \rho = 1$, $\epsilon = 0 \cdot 01$,

$$a^4 < \frac{64 \, (0 \cdot 002)^2 \, (20)^2}{50 \times 981} \times 0 \cdot 01,$$

i.e. $a < 0{\cdot}0120$ cm. [for $l = 20$ cm., $P = 50$ cm. water, $\eta > 0{\cdot}2$ cp.]
In many cases the viscometer will normally be required to deal with
much higher viscosities; but it is desirable to be able to make an
accurate re-determination of the viscosity of water at 20° C. so as
to allow the results to be compared with those of other observers.
For such a viscometer, with limits as above but minimum $\eta = 1{\cdot}0$
cp., the formula gives

$$a < 0{\cdot}0268 \text{ cm.}$$

If the length of the capillary is reduced below 20 cm., the maximum
permissible radius is also decreased according to (III. 2); but for
short tubes the criterion $l > 500\,a$ may demand a still smaller bore.
Thus, for the viscometer in which no liquid less viscous than water
at 20° C. is to be used, the maximum radius will be fixed by uncer-
tainty with regard to n rather than to m when the length is reduced
below 8·6 cm. $(a < 0{\cdot}0172$ cm.).

(2) Selection and calibration.

Having decided upon the maximum bore which the capillary
may have, it is next necessary to obtain a straight length of uni-
form tubing with a bore approaching this maximum. The use of
finer capillaries will involve not only increased difficulty in the
measurement of the radius but also greater liability to errors
caused by the possible presence of suspended matter in the liquids
examined. Thick walls are to be preferred, both for mechanical
reasons, to withstand strains imposed during grinding and in use,
and because the lumen tends to be more accurately circular than
that of thin-walled tubing owing, probably, to the action of surface
tension during the drawing of the tubes. When a batch of tubing
has been procured which has approximately the desired bore, a
preliminary calibration is made by means of a short thread of
mercury so that some lengths may be cut off which will show not
more than a slight conicality. From these a final choice may be
effected after examining, under the microscope, the shape of the
terminal cross-sections of some pieces a few centimeters longer
than will be required.

The selected portion is calibrated by the usual method of
measuring, with the aid of a travelling microscope, comparator
or projection apparatus, the length of a thread of mercury about
1 cm. long at different parts of the tube: a very detailed account
of the application of this method was given by Jaeger.[13] The

extreme positions of the mercury index or indices should be outside the portion of the tube which is to be used, so that the area of cross-section may be known right up to the ends when the tube is finally cut and ground. Suppose the calibration is performed by measuring the length of a thread which is moved from left to right, so that, in successive positions, the left-hand end of the thread lies in the plane occupied, in the previous position, by the right-hand end. Let the measured lengths be l_1, l_2, ... l_n, of which the mean is l_0, and the corresponding relative areas be A_1, A_2, ... A_n, of which the mean is A_0; it may be shown that these areas are given by

$$A_1 = A_0 (1+\delta_1)^{-1} \left\{ 1 - \frac{1}{n} \Sigma (\delta^2) \right\} \ldots \&\text{c.},$$

where $l_0\delta_1 = (l_1 - l_0) \ldots \&\text{c.}$

Now the fall in pressure in each portion of the tube will be proportional to l/A^2 if Poiseuille's Law holds; from the above equation we obtain analytically

$$\sum \left(\frac{l}{A^2} \right) = \frac{n l_0}{A_0^2} \left\{ 1 + \frac{5}{n} \Sigma (\delta^2) \right\} . \quad . \quad . \quad \text{(III. 3)}$$

A better method of treating the calibration data is to plot l/A^2 for each position of the index against the total distance of the midpoint of the thread from the first position of the left end of the index. If the tube has been marked and the distance from the first position to this mark is measured, it is then possible to obtain a planimetric integral for the value of the 'resistance' of whatever length is eventually left after the grinding has been finished.

(3) Determination of mean radius.

The areas of cross-section which are deduced from the above calibration are of course relative areas only and it is next necessary to determine the mean radius in terms of the standard metre. This is the crucial part of the standardization, since an error of 0·1 per cent. in the radius corresponds with an error of 0·4 per cent. in the viscosities which are to be calculated later. The method which has been employed by most investigators is to find the mass of mercury required to fill or nearly fill the capillary, the length of the column being determined as accurately as possible; it is convenient to perform these operations before the tube is cut, taking care that the thread of mercury occupies almost exactly the portion of the capillary which it is proposed to use. A small correction to the

measured length will normally be required, which may be deduced from the calibration curve. Needless to say, the tube must be cleaned and dried as thoroughly as possible before introducing the purified mercury. Bingham and White[14] tested for the presence of a film of moisture or of adsorbed gas on the walls by evacuating the tube after the length of the mercury column had been measured, and then moving the thread to and fro *in vacuo* so as to remove any entrapped film: they were unable to detect any change in the length. In view of the experiments of Manley[15] on the removal of the 'gas-grown skin' it appears that the test could be made more conclusive by passing an electrical discharge between the mercury and a second electrode *in vacuo*. The mass of the mercury is then found by transferring it to a small tared receptacle, making the usual buoyancy corrections. Since a tube such as was used by Thorpe and Rodger contains only some 13 mgm. of mercury it is necessary either to weigh on a micro-balance or else to refill the tube many times, measuring the length of each column of mercury, in order to collect several decigrammes which can be weighed on a balance sensitive to 0·01 mgm. or so. Corrections are required for the temperature at which the length was measured and for the volume of the mercury menisci; the latter may be estimated when the approximate mean radius has been calculated. The radius appropriate to the temperature at which viscosities are to be measured has finally to be corrected in accordance with the calibration data obtained in (2): the effective mean radius is always smaller than the mean radius deduced from the weight of mercury, as may be seen from equation (III. 3).

An alternative procedure for the determination of the mean radius, applicable when the tube has been cut and ground ready for use, is to measure the electrical resistance of a column of liquid which fills the capillary and wider vessels with which it communicates at each end. If mercury be used the radius so found will depend firstly on the accuracy with which the resistance can be measured and secondly on the evaluation of the ohm. There is little difficulty in measuring resistance with an accuracy as high as can be realized in the determination of the mass of the contents of the tube. The calculation of the radius from the length and resistance refers the result to the careful calibration and resistance measurements made in this and other countries on metre lengths of tubing of approximately 1 mm.² cross-section: owing to the

greater length and radius of the ohm tubes, the calibration and determination of mean area could be effected with greater accuracy than is likely to be attained by similar methods with tubes such as are needed for absolute viscometry.

The electrical method appears to have been first used by Merton.[16] Apparatus for the purpose was described by Higgins[17] who adopted a potentiometric arrangement which will be sufficiently indicated by inspection of Fig. 11. The presence of a film on the wall of the capillary would affect the result obtained in the same manner as in the weighing method. A check on the estimation might, however, be obtained by replacing the mercury by a
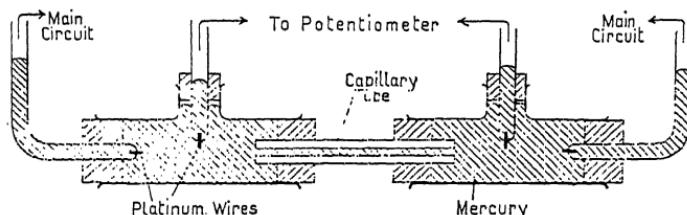
FIG. 11. Electrical resistance method for measuring mean radius.

solution of an electrolyte and making a conductivity determination using alternating current: the technique of such measurements has been so improved during the last decade that the convenience and accuracy are scarcely, if at all, inferior to those obtaining in direct-current work. It should be noted, however, that the effective length of the tube in these electrical methods is considered to be greater than the measured length by $1 \cdot 64a$: the value of the correction deduced mathematically by Maxwell and Rayleigh has been confirmed both for tubes containing mercury and for those filled with aqueous solutions (see Chap. II, §5).

Whereas the more usual procedure, involving a determination of the volume of mercury required to fill the capillary, furnishes the value of the integral of $A.\,dl$, the measurement of electrical resistance gives the integral of dl/A and is therefore more nearly related to the viscous resistance, which is the sum of terms of the form dl/A^2. The difference may be illustrated by a comparison of the effective mean values of A^2 calculated in the three cases for a uniformly conical tube, of a slope defined by $e = \dfrac{a_2 - a_1}{a_2 + a_1}$, where

a_1 and a_2 are the radii at the two ends: the means are proportional to $(1+\frac{2}{3}e^2)$, $(1-e^2)$ and $(1-\frac{10}{3}e^2)$ respectively.

(4) Correction for conicality.

Tubes are very frequently selected which are shown by calibration with a short mercury thread to be evenly conical, within the accuracy of measurement. For such capillaries the graphical integration described at the end of § 2 A (2) becomes superfluous, and may be replaced by the use of an expression for the mean radius which is due to Knibbs.[18] Let the conicality be defined by $r = a_1(1 + bx)$, where r is the radius at a distance x from one end at which it has the value a_1, and b is a constant; also let $r = a_2$ when $x = l$. If b is so small that the radial component of velocity is negligible, the fall in pressure over any small length dx will, on Poiseuille's law, be proportional to dx/r^4. The total fall in pressure between the two ends of the tube will therefore be proportional to

$$\int_0^l \frac{dx}{r^4} = \frac{1}{a_1^4} \int_0^l \frac{dx}{(1+bx)^4} = \frac{l}{a_1^4} \frac{(1+bl+\frac{1}{3}b^2l^2)}{(1+bl)^3}$$
$$= \frac{l}{3} \cdot \frac{a_1^2+a_1a_2+a_2^2}{a_1^3a_2^3}.$$

Hence a^4 in equation (II. 3, or 7) requires to be replaced by

$$\frac{3\,a_1^3a_2^3}{a_1^2+a_1a_2+a_2^2} \cdot \quad . \quad . \quad . \quad . \quad . \quad \text{(III. 4)}$$

Knibbs prefers to express the conicality by $e = (a_1-a_2)/(a_1+a_2)$ in which case, if $2a = a_1+a_2$, the simple Poiseuille equation becomes

$$\eta = \frac{\pi a^4 P}{8\,Ql}\left(1 - \frac{10}{3}e^2 + \frac{37}{9}e^4 - \ldots\right) . \quad . \quad \text{(III. 4 a)}$$

If, as is commonly the case, a has been derived from a measurement of the volume of the bore, rather than from direct observation of the diameters at the two ends, the correction factor must be modified to

$$\left(\frac{1-e^2}{1+\frac{1}{3}e^2}\right)^3 = \left(1-4e^2+\frac{20}{3}e^4 - \ldots\right) . \quad . \quad \text{(III. 4 b)}$$

It will be observed that the first power of e does not occur in any of the above expressions. Hemmy[19] raised objection to the total neglect of the radial velocities; by taking account of the variation of kinetic energy per unit volume along the tube he deduced a correction factor which amounts to $(1 - 2e)$, using Knibbs's

notation, when the velocity is such as to make the kinetic-energy correction small. Bond[20] in a criticism of Hemmy's paper and in a later paper of his own shows, however, that recalculation of the formula leads to a correction which is in fact negligible if the kinetic-energy correction is small and e is low enough that its square may be neglected.

(5) Correction for ellipticity of section.

The Poiseuille formula assumes that the cross-section of the tube is circular, a condition which is not true for such capillaries as are normally available. The shape of the end sections may be examined under the microscope, but it is difficult to obtain suitable contrast and illumination unless the glass is mounted, e.g. in Canada balsam; a procedure which has been adopted is to make slides from the adjacent ends of the tubing from which the selected length has been cut. Poiseuille, who gradually reduced the length of each capillary during the course of his experiments, was able to see how the shape varied from place to place, but with a tube which is to be preserved for use it is necessary to assume that the shape is the same as that at the ends or varies uniformly from one end to the other. The assumption may be verified approximately by examining the tube when it is immersed in a medium having the same refractive index as the glass or by taking an X-ray photograph of a mercury thread as described by Anderson and Barr[21]: but the precision obtainable is not high.

In general, the major and minor axes of the terminal cross-sections will not be at right angles, but it is usual to assume for the purpose of the correction involved that the shape is that of an ellipse having these axes. The equation for the rate of flow through a tube of elliptical cross-section may be obtained quite readily from the definition of the coefficient of viscosity, in a manner analogous to that given in Chapter II §3 for a circular tube, by evaluation of the double integral which results from the introduction of the equation of the ellipse. The solution shows that a^4 of equation (II. 3) must be replaced by

$$\frac{2\,b^3c^3}{b^2+c^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(III. 5)}$$

if b and c are the semi-axes of the ellipse. This result was first obtained by Mathieu.[22] It was pointed out by Knibbs[23] that if the ellipticity, defined by $\epsilon = (b - c)/(b + c)$, be small the rate of flow,

calculated for a circle of mean radius $a = \frac{1}{2}(b + c)$, may be corrected by multiplying a^4 by

$$(1 - 4\,\epsilon^2 + 7\,\epsilon^4 - \ldots). \quad . \quad . \quad . \quad . \quad \text{(III. 5 a)}$$

When the tube is both conical and elliptical, equation (III. 4 a) thus becomes

$$\eta = \frac{\pi a^4 P}{8\,Ql}\left(1 - 4\epsilon^2 - \frac{10}{3}e^2\right), \quad . \quad . \quad . \quad \text{(III. 6)}$$

where ϵ^2 may be given a value which is the mean of those found for the two ends. The formula shows that the error produced by neglect of the corrections is very small provided the differences between the four semi-axes are not excessive: a difference of about 3 per cent. between the semi-axes at each end or between the mean radii of the two ends causes an error of only 0·1 per cent. in a viscosity determination.

The corrections given by equation (III. 6) for deviation of the shape of the bore from that of a right circular cylinder apply strictly only when the mean radius is deduced from direct linear measurements. They have frequently been quoted and used as if they were equally applicable when the mean radius is deduced, as it usually is, from the volume of mercury required to fill the tube. If the radius a is that of a circular cylinder having the same volume as the experimental capillary, the equation becomes (cf. Knibbs[23])

$$\eta = \frac{\pi a^4 P}{8\,Ql}\,(1 - 2\,\epsilon^2 - 4\,e^2). \quad . \quad . \quad \text{(III. 6 a)}$$

By way of illustration of the lack of uniformity of bore, which has been considered to be tolerable by various experimenters, the following examples of recorded measurements may be cited:

	Length.	Mean diameter.	ϵ_1	ϵ_2	e
	cm.	mm.			
Poiseuille . .	10	0·142	0·007	0·009	0·004
,, . .	10	0·113	0·009	0·008	0·004
Thorpe & Rodger .	4·9	0·164	0·031	0·025	0·003
Bénard . .	44	0·140	0·05	0·04	0·002
Bingham & White .	9·4	0·246	0·002	0·006	0·002

In the above table ϵ_1 and ϵ_2 represent the ellipticities, defined as above, of the two ends and e the difference between the mean radii of the ends relative to the diameter. It will be observed that the

errors due to these divergences, calculated by the formula given, are small in every case, amounting for only one tube to as much as 0·4 per cent. The fact that ϵ is always greater than e results presumably from the circumstance that although preliminary calibrations allow the investigator to select a tube having a fairly uniform area of cross-section from one end to the other, no convenient method has been available to give an estimate of the ellipticity until the tube has been cut to the length required.

It may be well to remark that the equation for the rate of flow through a tube of elliptical cross-section assumes that the major axes remain in the same plane from one end of the tube to the other. This condition has not usually been shown to be true, and it is obvious that if rotation of the axes occurs, the resulting rotation of the stream lines will produce an increase in the resistance offered by the tube. The magnitude of this effect has not been calculated, but errors are not likely to arise from it if the usual ellipticity correction does not itself amount to as much as 0·1 per cent., except possibly at higher velocities of flow than are here contemplated.

The effect of ellipticity on the magnitude of the kinetic-energy correction has been invariably ignored. It may be shown, by a method entirely analogous to that given in Chap. II, §4, but complicated by the insertion of the equation of the ellipse, that the kinetic-energy term of the modified Poiseuille equation becomes

$$\frac{m\rho Q}{8\pi l} \cdot \frac{bc}{\frac{1}{2}(b^2+c^2)} \left[\text{instead of } \frac{m\rho Q}{8\pi l}\right], \quad . \quad . \quad \text{(III. 7)}$$

the coefficient m having the same value ($=$ unity, to a first approximation). Assuming that the 'mean radius' has been determined by weighing the mercury required to fill the tube, the usual kinetic-energy term should therefore be corrected by multiplying it by the factor $(1 - 2\epsilon^2)$. The correction of course is negligible in such absolute measurements as are considered in this chapter, when the kinetic-energy term is itself small and ϵ is also small; but there may be some occasions when the effect should be noted. Thus, in the construction of viscometers for purely relative measurements, in which high velocities are sometimes tolerated and little care is usually taken to avoid ellipticity, the correction may become appreciable; since the mean radius is then virtually determined from the viscosity of a calibrating liquid, the correcting factor is actually reduced to $(1-\epsilon^2)$.

(6) Measurement of length.

The procedure adopted by Bingham and White in the preparation of the ends of the tubes is detailed in their paper.[24] It is of course convenient to make use of a standard taper for the ground joints by which the capillary is attached to the vertical arms of the viscometer, so that different capillaries may be interchangeable; but it is more important that the fit shall be as perfect as possible. The ends should be ground plane and at right angles to the axis, chipping of the extremities of the bore being avoided by plugging them with wax or fusible metal. The accuracy required in the measurement of the length is fairly easily obtainable, and errors in this determination should be negligible compared with those attaching to the estimation of the mean radius.

(*B*) *The pressure system.*

(1) Maintenance of constant pressure.

The simplest method of maintaining a nearly constant excess pressure above the liquid in one arm of the viscometer is to make connexion, via a stop-cock, with a large reservoir into which air can be forced by means of a pump. If the volume of the viscometer bulb does not exceed 10 ml., a reservoir having a capacity of 10 litres should be sufficient to make the initial and final applied pressures differ by less than 0·1 per cent. If the time of flow is long, variations in temperature of the reservoir may, however, produce more considerable changes between the beginning and end of a run; these are minimized by suitable lagging. An empty oil drum may readily be adapted to serve as a reservoir and is of a convenient shape for the application of insulation.

Various arrangements incorporating constant-level devices, Mariotte bottles, &c. have been adopted by different experimenters in order to ensure absolute constancy of pressure (cf. Pribram and Handl[25]). A convenient manostat is described by Erk[26] in which water from a 'chicken-feed' constant level is supplied to and overflows from a cylinder standing in a large corked tubulated bottle, from which the excess may be run off when necessary. A very similar arrangement was used by Wiedemann[27] in his earliest experiments. A form suitable for pressures up to 2 or 3 feet of water, which may be constructed from stock apparatus in any laboratory, is illustrated in a note by Gray.[28] If the expansion of the air due to rise in temperature is more rapid

than the flow of liquid through the viscometer, these apparatus, like many of their predecessors, allow an increase in pressure to occur. The writer has used a method in which the pressure in a large reservoir is maintained by means of a cylinder of compressed air; the valve is adjusted so that bubbles escape slowly and continuously from a tube which branches from the connexion between the cylinder and the reservoir and dips to the required depth into water. Damping of the inevitable small fluctuations of pressure due to the formation and release of bubbles may be effected by the interposition of a short length of capillary tubing or, preferably, of a tightly packed cotton-wool filter-tube between the bubbler and the reservoir (see Fig. 12). If the required pressure is more than some two or three metres of water, a number of bubblers in series may be used; Bingham[29] gives a diagram of a multiple tube regulator recommended for this purpose. For pressures up to two atmospheres he prefers, however, to let the excess air bubble from a tube of 5 mm. diameter dipping into mercury in a single long one-inch iron pipe; with such arrangements it is difficult to avoid a somewhat jerky escape of bubbles.

FIG. 12.   Regulation of pressure by bubble method.

In a recent paper Rhodes and Hodge[30] describe a method which makes use of the pressure of the water main to obtain the air pressure required: the water is admitted to the air reservoir and escapes continuously from an overflow tube leading from the bottom of the reservoir to the required height. As figured in their paper, the device allows some small variations in pressure to occur, but a modification, of which the principle is shown in Fig. 13, should give absolute constancy: with the exception of the gauge tube GG, which is of glass, the whole construction may be of metal and may be soldered or screwed at X into any convenient reservoir.

A drip of water is allowed to occur from the cock O and the supply is adjusted so that a trickle escapes from the overflow shown at the top or through the mercury in M; alternative fixed or adjustable overflows for intermediate pressures may be attached at N. When high pressures are to be used air may be introduced through the tyre valve P in order to avoid the introduction of much water into the reservoir vessel.

To manometer
and viscometer
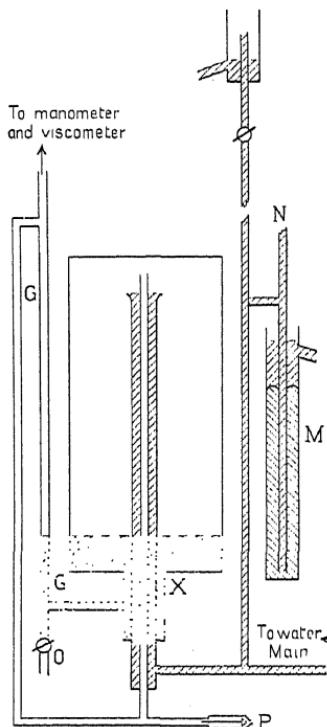
FIG. 13. Scheme for obtaining a constant pressure of air by means of the water main.

A method differing in principle from all the foregoing was used with Stone's viscometer[31] to maintain a constant excess pressure of air during an experiment. Two similar cylindrical bulbs (see Fig. 14) were connected by a siphon and rubber tubing and contained mercury; the lower bulb F was fixed in position and the upper bulb G was suspended from a spring: the extensibility of the spring was arranged to be such that when a volume of mercury Al (A = area of cross-section of each bulb) flowed from the upper to the lower bulb, the spring contracted in length by an amount equal to $2l$. This system provides a compact and self-contained pressure regulator and should give very constant pressures if the mechanical details are correct. It is stated that a similar arrangement, in which G was a tube of three inches diameter and contained water instead of mercury, could be adjusted so that the head of water remained constant to 0.005 mm. For the production of different constant pressures it might be convenient to make preliminary adjustments of the mass of air above the mercury in F by a three-way tap in place of that shown. The same principle was elaborated by Hyde[32] in a viscometer designed for tests on oils at high pressure, in which the constant driving pressure was secured by means of mercury in direct contact with the oil.

The air (or nitrogen) pressures obtained by any of these devices are applied to either arm of the viscometer by manipulation of two

three-way cocks so that when one limb is in communication with
the source of pressure the other is open to the
atmosphere. It is usually desirable to insert
calcium chloride guard-tubes with cotton-wool
filters to prevent access of moisture or dust
from the pressure reservoir or from the air;
when volatile liquids are under examination a
small bulb containing a few drops of the liquid
(or solvent) may be attached to each arm to re-
duce diffusion of vapour from the viscometer.
The stop-cocks, guard-tubes and other con-
nexions between the viscometer and the mano-
meter or the atmosphere must offer a negligible
resistance to the flow of gas through them at
the highest velocity contemplated.

(2) Corrections to the manometric pressure.

The pressures are usually read on a water or
mercury manometer of which one arm is open
to the air. It is frequently recommended that
the limbs be so bent that the parts into which
the liquid menisci will be displaced shall lie in
the same vertical line: this allows the use of a
single scale for reading the positions. Reference
may be made to general text-books for discus-
sion of the errors due to height of meniscus,
&c. and of the methods of correction for tem-
perature of the water or mercury and of the
scale. The density to be used in converting the
observed heads to gm. per cm.^{2} is obviously
the apparent density in air; i.e. the density in
gm. per ml. at the temperature of observation,
as obtained from tables, requires to be dimin-
ished by some 0·0012 gm. per ml. Two other
corrections were applied by Poiseuille: (a) for
the difference between the atmospheric pres-
sures at the levels of the liquid in the open

FIG. 14. Stone's
pressure regulator
(after the figure in
Engineering).

arms of the manometer and of the viscometer: the barometric
pressure falls by 0·13 cm. of water for an ascent of 100 cm.;
(b) for the difference between the pressures of the compressed air at

the levels of the liquids in the communicating limbs of the mano-
meter and viscometer: the difference is the weight of a column of
air of height equal to this difference in level and under a pressure
equal to the sum of the barometric and manometric pressures.

These corrections are explained and discussed by Bingham and
Jackson.[33] Their analysis shows that if h is the height read on the
manometer, the liquid in which has the density ρ, the excess p
above atmospheric pressure acting on the surface of the liquid in
the viscometer is given by

$$\frac{p}{g} = h\,(\rho - \sigma) - \frac{\sigma}{2}\frac{h^2\rho}{1033} - h'\sigma\frac{h\rho}{1033}, \quad . \quad . \quad \text{(III. 8)}$$

where σ is the density of the ambient air and h' is the vertical
distance of the middle of the viscometer above the middle of the
manometer. The last term amounts to only $0\cdot02$ gm. per cm.[2]
when $h' = 50$ cm. and $h\rho = 300$ gm. per cm.[2]; hence it may be
made negligibly small by placing the manometer so that its zero
is approximately level with the viscometer bulbs.

(3) Corrections to pressure in the viscometer.

The foregoing equation (III. 8) states the value of the gaseous
excess pressure applied to the surface of the liquid in one arm of
the viscometer. The mean effective pressure difference producing
the flow through the capillary differs from this value owing (a) to the
surface tension, (b) to the hydrostatic head of the liquid under test.

(a) *Capillarity correction.* The surface tension of the liquid tends
to raise or depress the meniscus, according as the liquid wets or
does not wet the wall. If the two 'bulbs' of the viscometer are of
uniform bore, as in Stone's apparatus, the capillarity correction is
the same for all positions of the two menisci and becomes zero if
both bores are identical. If the measuring bulb has the conven-
tional form in which the diameter is considerably reduced at and
near the fiducial marks, the correction may be relatively large at
the beginning and at the end of the flow. If the recipient bulb were
an exact counterpart of the measuring bulb and the working
volume were so adjusted that the menisci were in corresponding
positions at every stage of the flow, the effects of surface tension
would be equal and opposite. But these conditions cannot be ful-
filled in practice, and it is therefore necessary to estimate the
correction required.

Owing to the probable irregularity of blown glass bulbs it would not be entirely satisfactory to calculate the average capillary rise even if the further calculation were straightforward. Poiseuille recognized that in his apparatus, in which the recipient was the thermostat itself, the capillarity correction might be important. He obtained an estimate of the correction by comparing the rates of flow of water from the measuring bulb and from a vertical cylindrical tube, of known bore, through the same capillary and under the same head. Since the effect of surface tension in the cylindrical tube could be deduced from the diameter he was able to calculate the correction for the bulb by assuming that the rate of flow was proportional to the applied pressure *minus* the correction. For the smallest bulb used by Poiseuille (volume 0·125 cm.³) the correction amounted to 10 mm. of water; for a 2 cm.³ bulb it was 3·2 mm.

A graphical method was used by Bénard[34] in his experiments with mercury. He determined first the capillary depression for various positions of the meniscus in the bulb, by direct comparison of the level with that in a wide vertical tube communicating with the bulb. Next the variation of the level with time was observed during an experiment in which a constant external pressure was applied to drive the mercury through the viscometer. Hence he was able to plot the depression due to surface tension as a function of time; by integration of the curve he obtained a value 0·31 mm. of mercury as the mean correction by which to increase the applied pressure for a 4 cm.³ bulb delivering mercury.

From a consideration of the arguments advanced in the next paragraph it will be recognized that neither of these experimental methods gives an exact value for the capillarity correction unless the variations in hydrostatic pressure in the viscometer are also taken into account. The correction is not strictly constant but is dependent on the applied pressure, and the inconstancy may become important if the applied pressure be low.

(b) *Correction for hydrostatic head in the viscometer*. The actual pressure effective in producing flow through the capillary at any moment is the sum (corrected for surface tension) of the excess gaseous pressure applied to one surface of the liquid and the hydrostatic pressure due to the difference in level between the free surfaces. Now the levels of liquid in the two arms of the viscometer

are necessarily varying during an experiment, and a mean value must therefore be used to find the mean effective pressure. Poiseuille showed that under the conditions of his experiments it was sufficiently accurate to add to the manometric pressure the arithmetic mean of the initial and final heads in the viscometer. But it was shown by Koch,[35] for a case in which the externally applied pressure was zero, that the mean hydrostatic head was not equal to half the sum of the initial and final heads; his calculation has been overlooked by many later investigators, some of whom have made the mistake to which he drew attention. The value of the mean head was derived anew by Meissner,[36] in a discussion of the Engler viscometer, by Simeon,[37] by Bingham, Schlesinger, and Coleman,[38] and by Lidstone.[39]

In the simplest calculation it is assumed that each of the vessels from and into which the flow occurs is of constant cross-section. Let the areas of cross-section of the two vessels be A_1 and A_2 and let the initial and final heads be x_1 and x_2; the total volume discharged is therefore equal to

$$\frac{A_1 A_2}{A_1 + A_2} (x_1 - x_2).$$

If the constant applied pressure be p_0 and the hydrostatic head at any time t during the flow be x, the effective pressure producing flow at that time is $(p_0 + x \rho g)$, where ρ is the density of the liquid in the viscometer. Assuming Poiseuille's Law, we may state the rate of discharge at time t as

$$\frac{A_1 A_2}{A_1 + A_2} \cdot \frac{dx}{dt} = k (p_0 + x \rho g),$$

where k is a constant. Integration between the limits $t = 0$, $x = x_1$ and $t = t_2$, $x = x_2$ gives

$$k t_2 = \frac{A_1 A_2}{A_1 + A_2} \cdot \frac{1}{\rho g} \cdot \log_e \frac{p_0 + x_1 \rho g}{p_0 + x_2 \rho g}.$$

But if P is the mean effective pressure we have also

$$\frac{A_1 A_2}{A_1 + A_2} \cdot \frac{x_1 - x_2}{t_2} = kP,$$

so that

$$P = \frac{(x_1 - x_2) \rho g}{\log_e \dfrac{p_0 + x_1 \rho g}{p_0 + x_2 \rho g}}. \qquad . \quad . \quad . \quad . \quad \text{(III. 9)}$$

The arithmetic mean between the pressures effective at the beginning and at the end of the flow is, of course, $p_0 + \frac{1}{2}(x_1 + x_2)\rho g$.

Special forms of equation (III. 9) have been obtained by making various assumptions. Thus, when the two reservoirs are of equal cross-section ($A_1 = A_2$) and of length h, and their midpoints are at the same level to which the liquid is filled, so that the arithmetic mean pressure is p_0, the equation becomes

$$P = \frac{0 \cdot 8686\, h\rho\, g}{\log_{10} \dfrac{p_0 + h\rho\, g}{p_0 - h\rho\, g}}$$

as given by Bingham, Schlesinger and Coleman;[38] if there is a vertical distance x_0 between the centres of the bulbs, it is necessary to substitute $p_0 \pm x_0 \rho\, g$ for p_0 in this expression. Meissner's formula for the mean hydrostatic pressure during discharge from an open cylindrical cup through a capillary into the air is

$$P = \frac{0 \cdot 4343\,(x_1 - x_2)\rho\, g}{\log_{10} x_1/x_2} \quad . \quad . \quad . \quad . \text{(III. 9 a)}$$

The corresponding formula for the discharge of the contents of a spherical bulb of radius a, of which the centre is at a height h_0 above the exit end of the capillary, is given by Barr[40] as

$$P = \frac{\frac{4}{3}a\rho\, g}{2\,c - (c^2 - 1)\log_e \dfrac{c+1}{c-1}}, \quad \text{where } c = \frac{h_0}{a} \ . \ \text{(III. 9 b)}$$

The accompanying table, calculated by Lidstone[39] for bulbs of uniform bore, illustrates the importance of the logarithmic head correction at low pressures and the rapidity with which the effective mean pressure approaches the arithmetic mean as the variation in head during the flow is reduced. The first column A, gives the ratio of the initial to the final effective pressure, the second column B, the ratio of the arithmetic mean pressure to the difference between the initial and final pressures, and the third column C the ratio of the arithmetic mean pressure to the corrected or effective mean pressure.

$$A = \frac{p_0 + x_1 \rho\, g}{p_0 + x_2 \rho\, g} = \frac{h_1}{h_2}; \qquad B = \frac{\frac{1}{2}(h_1 + h_2)}{h_1 - h_2}$$

$$C = \frac{\frac{1}{2}(h_1 + h_2)\log_e h_1/h_2}{h_1 - h_2}$$

A	B	C
9	$\frac{5}{8}$	1·3733
5	$\frac{3}{4}$	1·2071
3·6	$\frac{7}{8}$	1·1369
3	1	1·0986
2	$1\frac{1}{2}$	1·0397
$\frac{5}{3}$	2	1·0186
$\frac{7}{5}$	3	1·0094
$\frac{9}{7}$	4	1·0052
$\frac{21}{19}$	10	1·0008
$\frac{41}{39}$	20	1·0002
$\frac{61}{59}$	30	1·00015

Bingham, Schlesinger, and Coleman suggest that in the design of an 'absolute' viscometer of the type illustrated in Fig. 8 the height of the bulbs should be less than one-thirtieth of the lowest head (of water) which is proposed to be applied: if this precaution be adopted, making $B = 15$ in the above table, the correction to the arithmetic head is less than 0·05 per cent. and may be neglected.

In the derivation of equation (III. 9) it was assumed that the kinetic-energy correction was negligibly small. In most of the technical viscometers which will be described in the next chapter the kinetic energy may be considerable and the initial head much greater than the final head. For the theory of such instruments equation (III. 9) is therefore not adequate; von Mises[41], Lidstone[42] and Dryden[43] have worked out an equation which may be cited here, for comparison with Meissner's, in a form similar to that used by Herschel and Bulkley.[44] With our notation, the mean effective head $P/\rho g$ becomes

$$\frac{P}{\rho g} = H + \tfrac{1}{4} CH^2, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(III. 10)}$$

where
$$H\left(\log_e y_1/y_2 + y_1 - y_2\right) = x_1 - x_2,$$
$$1 + y_1 = \sqrt{(1 + Cx_1)},$$
$$1 + y_2 = \sqrt{(1 + Cx_2)},$$
$$C = \frac{mg\rho^2 a^4}{16\,\eta^2 l^2}.$$

I have found that the cumbersome definition of H in this equation may be replaced, when the flow is not too rapid, by the simpler approximate definition

$$H \log_e\left(\frac{x_1}{x_2} \cdot \frac{1 + \tfrac{1}{4} Cx_1}{1 + \tfrac{1}{4} Cx_2}\right) = x_1 - x_2.$$

The error in this approximation is less than 0·05 per cent., so long as the kinetic energy is not more than one-tenth of the viscous resistance at the beginning of the flow. (Cf. Heydwiller[45] and Bridgman[46]).

In few accurate absolute viscometers, however, are the measuring bulbs of uniform cross-section or even of any simple geometric form. As regards instruments with which we are here concerned, the equations above mentioned will therefore serve chiefly for purposes of design. To obtain an accurate value for the mean hydrostatic head it is necessary to resort to experiment. In connexion with the examination of the behaviour of Ostwald viscometers, Grüneisen[47] and Applebey[48] measured the mean hydrostatic head by the following method. They noted (i) the actual hydrostatic pressures, as registered by an attached manometer, corresponding with different positions of the menisci between the upper and lower extremes, and (ii) the times required for these positions to be reached when the liquid ran out under its own head. Combination of the two series of results gave a curve showing the variation of hydrostatic head with time, from which a mean hydrostatic head could be deduced. An analogous method was used by Thorpe and Rodger[49] in their classical work. Applebey states that the mean so obtained 'differs from that calculated from the difference of level at mean time, owing to the surface effects' and proceeds to calculate from the discrepancy a factor to be used in correcting for the variation of capillary elevation with different liquids. In this method the determination (ii) is necessarily less exact than the measurement of the time of flow of the total volume, but there is also an error of principle involved in the application of the results when externally produced pressures are added to the hydrostatic pressure of the liquid in the viscometer. As may be seen from comparison with Koch's equation, the 'mean hydrostatic pressure', by which the mean pressure effective in producing flow exceeds the applied gaseous pressure, is not a constant but increases as the externally applied pressure increases.

The method suggested by Bingham, Schlesinger and Coleman[50] for the evaluation of the hydrostatic pressure operative in a viscometer of the type shown in Fig. 8 consists in observation of the times t_1 and t_2 required to empty and to fill the measuring bulb, when the same excess pressure p_0 is applied to the left and right limbs respectively of the viscometer containing the normal working

volume of a liquid of known kinematic viscosity, η/ρ. If the required hydrostatic head be x_0, the total pressure operative when the bulb is being emptied is $p_0 + x_0\rho g$ and that operative when the bulb is being filled is $p_0 - x_0\rho g$. If the modified Poiseuille equation (II. 7 a) be written

$$\eta = KPt - K_1\rho/t, \quad . \quad . \quad . \quad . \quad \text{(III. 11)}$$

where $K\left(= \dfrac{\pi a^4}{8V(l+na)}\right)$ and $K_1\left(= \dfrac{mV}{8\pi(l+na)}\right)$ are constants

involving the dimensions of the viscometer, we have

$$p_0 + x_0\rho g = (\eta + K_1\rho/t_1)/Kt_1,$$
$$p_0 - x_0\rho g = (\eta + K_1\rho/t_2)/Kt_2;$$

whence
$$x_0 = \frac{\eta}{2K\rho g}\left(\frac{1}{t_1} - \frac{1}{t_2}\right) + \frac{K_1}{2Kg}\left(\frac{1}{t_1^2} - \frac{1}{t_2^2}\right). \quad . \quad \text{(III. 12)}$$

When the kinetic-energy term $K_1\rho/t$ is small, it is obviously sufficiently accurate to simplify this equation to

$$x_0 = \frac{\eta}{2K\rho g}\left(\frac{1}{t_1} - \frac{1}{t_2}\right)$$
$$= \frac{p_0}{\rho g} \cdot \frac{t_2 - t_1}{t_2 + t_1}.$$

In the foregoing argument it is assumed that x_0 has the same value for both directions of flow, and it would follow that the value would become zero if the bulbs were exactly similar and at the same level. It is obvious, however, from inspection of the table on p. 76, that the mean hydrostatic head may amount, e.g. to some 0·5 per cent. of p_0 if the bulbs are of such length as to make the effective pressure at the beginning of the flow differ from that at the end by as much as $\frac{1}{4}p_0$. The existence of such a hydrostatic head would not be revealed by timing the flow in both directions, since with an exactly symmetrical arrangement of the bulbs the two times would be identical. The duplication of the test therefore reveals and estimates only an actual dissymmetry between the two limbs of the viscometer, and to make the logarithmic correction negligible it is necessary to employ a suitably high external pressure. The criterion suggested on p. 76 is usually adequate, but it should be remembered that the variation in pressure during an experiment is proportional to the density of the liquid in the viscometer; a minimum applied pressure which is satisfactory for tests on water is likely to be too low for tests on mercury. If the required conditions are not fulfilled it will be

necessary to find the mean effective pressure by a method analogous to that of Grüneisen but with a constant externally applied pressure equal to that which is to be used; with viscometers of the usual type the precision attainable would be low.

The hydrostatic-head correction found by the method of reversal of flow includes the correction due to differences between the effects of surface tension produced by lack of symmetry of the two reservoirs. When equation (III. 12) has been used to determine the head it is therefore necessary to obtain an estimate of the capillarity correction if the viscosities of liquids of very different surface tension are to be measured. If we write

$$x_0 \rho\, g = h^1 \rho\, g + C \gamma,$$

where h^1 is the hydrostatic head which would be obtained by elimination of the effects of the surface tension γ, and C is also an instrumental constant, it is obviously possible to determine h^1 and C by making observations of the times of filling and emptying of the bulb with two liquids for which ρ and γ are known. The liquids selected should be such that the ratio of densities is very different from the ratio of surface tensions. This repetition of the calculation of x_0 should not be omitted when the viscometer contains bulbs of small bore, even if the first experiments indicate a low value for x_0, since $h^1 \rho\, g$ and $C\gamma$ may happen to be nearly equal and opposite.

(C) *Volume of the measuring bulb.*

(1) Selection.

The volume of the measuring bulb must bear a certain approximate relation to the length and bore of the selected capillary, if the time of flow of the least viscous liquid which will be used is to be within certain limits. Since the time of flow is normally read on a stop-watch reading to 0·2 sec., errors approaching 0·1 per cent. will not be avoided unless the minimum time is 200 sec. Although considerably higher precision might be obtained by means of a recording chronograph, it would still be advisable not to reduce this minimum very far owing to the likelihood of accentuating drainage errors. We have already obtained estimates (§ 2 A (1)) for the maximum diameter of the capillary tube by making certain assumptions: it will be useful to calculate a minimum for the volume of the bulb by adding to these assumptions the above-

mentioned time. We thus find, with $P = 50$ cm. of water and $l = 20$ cm.,

$$V \nless ca.\ 2 \text{ cm.}^3 \text{ for } \eta \nless 0{\cdot}2 \text{ cp. } (a = 0{\cdot}0120 \text{ cm.});$$

$$V \nless ca.\ 10 \text{ cm.}^3 \text{ for } \eta \nless 1{\cdot}0 \text{ cp. } (a = 0{\cdot}0268 \text{ cm.}).$$

Restriction of the length of the capillary to 10 cm. instead of 20 cm. would reduce these minimum volumes to one quarter, since the maximum permissible radius is proportional to $\sqrt{l}$.

Even with the smallest of these suggested volumes it is only necessary to make the constrictions above and below the bulb to a diameter of abour 3 mm. in order to read the volume with an accuracy of 0·1 per cent. We shall find reasons later, however, (§ 2 C. (3)) for preferring volumes larger than the minima above specified.

(2) Measurement.

The volume of the measuring bulb is usually determined by weighing the mercury required to fill it. The graduation marks etched on the constrictions should extend completely round the glass and should lie in planes at right angles to the axis of the tubing. It is desirable that the calibration be effected while the viscometer is in course of construction, at a stage when a stop-cock can be sealed on and removed conveniently, e.g. before the ground joint is prepared in the form illustrated on p. 53. If the apparent weight in air of the mercury which fills the bulb at $t°$ C. is M gm., the capacity V at $15°$ C. is given by

$$V = M \times \frac{0{\cdot}999943}{\delta} \{1 + \alpha\,(15 - t)\},$$

where δ is the density of the mercury at $t°$ C. and α is the coefficient of cubical expansion of the glass. A table of values of the factor multiplying M, calculated for temperatures from $5°$ C. to $30°$ C. assuming $\alpha = 26 \times 10^{-6}$, is given by Stott.[51] In this and some similar tables the volumes are in millilitres; for the purpose of absolute viscometric determinations the volumes should, strictly, be expressed in cubic centimetres, as will be realized from the method of derivation of Poiseuille's formula: but the difference is beyond the precision of present-day viscometry (1 ml. = 1·000028 cm.³).

(3) Drainage error.

The accuracy attainable in the determination of volume by weighing the content of mercury is higher than can be reproduced

in the normal use of the viscometer, owing to the effects of the film left on the walls when the working liquid is one which wets the glass. Thorpe and Rodger estimated that the error when using water in their viscometer was approximately 0·1 per cent. The shape of the lower end of the measuring bulb is copied, in Bingham's viscometer, above the upper constriction in the hope that the rates of drainage from the walls will be approximately the same when the meniscus is passing the upper and lower marks. It is a virtue of the method of determination of the mean hydrostatic pressure by reversal of the direction of flow (§ 2 B (3) b) that a repetition of the determination using the same applied pressure with a more viscous liquid, enables the observer to detect any considerable *differences* in the drainage error; the ratio between the times of emptying and filling of the bulb will obviously vary if the volumes adhering to the walls are not the same for two liquids, and some interval is allowed for drainage to occur between the observations.

It was pointed out by Herschel[52] that even the precautions adopted in the design of Bingham's viscometer were insufficient to avoid the possibility of appreciable error when viscous liquids were driven through the instrument fairly rapidly by the application of high pressures. Bingham and Young[53] made a series of measurements of the volumes discharged from a bulb of the recommended shape, by weighing the liquid forced out through a capillary by various constant pressures in the interval between the passage of the meniscus past the two marks. Using castor-oil at 20° C. in a 24-ml. bulb they found, for example, an error of 1·4 per cent. when the bulb was emptied in 7·8 min., of 0·9 per cent. for 18 min. and of 0·5 per cent. for 48 min. They concluded that the error was directly proportional to the viscosity and gave a table for the errors corresponding with various viscosities and rates of discharge. The table applies apparently to the same bulb, and the errors would presumably be relatively larger for smaller volumes.

The paper of Bingham and Young contains no data proving that the error is directly proportional to the viscosity. An analysis of the problem of the retention of liquid by a solid surface was given by the Research Staff of the General Electric Co., Ltd., of London.[54] These authors show that for the simple case of a flat slab of solid being drawn vertically with velocity v through the surface of a

liquid of viscosity η and density ρ, the thickness x of the adherent film is approximately

$$x = \sqrt{\frac{2 v \eta}{9 \rho g}} \quad . \quad . \quad . \quad . \quad \text{(III. 13)}$$

They give reasons for supposing that a similar formula, independent of surface tension to a first approximation, holds for the case of a liquid falling inside a tube. It is assumed in their argument that the subsequent drainage of the film may be neglected, e.g. that the film is chilled or evaporated to a stiff consistency not far from the surface. The conditions in the use of a viscometer do not allow us to make such an assumption, and the rate of reduction in thickness of the film will evidently also be a function of the viscosity. A formula is given by Wartenberg and Pertzel[55] for the thickness x of the film retained on a vertical surface of height h after draining for a time t: according to this formula

$$x^2 = \frac{3 x_0^2 \eta h}{3 \eta h + 2 x_0^2 \rho g t}, \quad . \quad . \quad . \quad \text{(III. 14)}$$

where x_0 is the initial thickness. Although neither this nor the previous equation can be applied quantitatively to estimate the drainage error of a viscometer bulb, it seems reasonable to assume that the error tends to vary not with the viscosity itself but with the square root of the viscosity.

In this connexion reference may be made to experiments by Stott on the effect of rate of delivery on the quantities of water retained on the walls of a pipette,[56] or of a burette.[57] Stott's curves are fairly consistent, except at the highest speeds, with an assumption that the thickness of the adhering film varies with the square root of the rate of discharge and also therefore, according to the theory of dimensions, with the square root of the viscosity.

From the foregoing discussion it would appear to be necessary, for precise viscometry, to supplement the determination of the content of the bulb by means of mercury with measurements of the volumes of various liquids discharged from the bulb at different rates of efflux. The procedure adopted by Bingham and Young would not be convenient for volatile or hygroscopic liquids and it requires an accurate determination of the density of each liquid used. A more widely applicable method might be found by temporarily attaching below the bulb a mercury reservoir and a capillary so that the volumes could be determined by weighing

not the liquid itself but the mercury which it displaced from the reservoir. An investigation into the thickness of the film retained on the walls of cylinders of various diameters, when liquids of widely differing viscosities and surface tensions are discharged at high and at low speeds, suggests itself as being not only of general interest but as likely to establish relationships which might lead to simplification of the calibration of viscometers, pipettes, &c.

The occurrence of appreciable error in viscosity determinations made with a viscous liquid in a completed viscometer may be detected either by the change in the ratio between the times of emptying and filling of the bulb from that found with water (p. 78), or by a difference in the viscosity calculated from observations with widely different applied pressures.

3. Some practical details.

(A) *The filling of the viscometer.* Since the capillary has a diameter of the order of 0·1 mm. it is essential, if an accuracy of 0·1 per cent. is to be ensured, that neither the viscometer nor the liquid introduced into it shall contain solid particles, droplets of an immiscible liquid, or bubbles of gas having dimensions comparable with one four-thousandth of 0·1 mm. Otherwise, there is a possibility that these foreign bodies may lodge in the capillary and cause a virtual reduction in its diameter. Particles having a diameter of 25 $\mu\mu$. are, however, invisible even under a microscope, and it is impossible to demonstrate their absence from the viscometer. Investigators have therefore been obliged to regard concordance between duplicate determinations of viscosity as the best proof of the homogeneity of their material and to assume that abnormally long times of flow are due to obstruction of the capillary. The most successful experimenters have taken elaborate precautions to avoid such obstruction. The viscometer is carefully cleaned: if oils or other organic materials have been in contact with the interior, a suitable solvent is first added to remove them as completely as possible and the solvent is washed or drained out. The residual contamination may usually be removed by filling the instrument with a prepared mixture of equal volumes of strong sulphuric acid and of a saturated solution of potassium bichromate and standing over night. A new viscometer may contain fragments of glass which are not removable by such treatment and require to be detached by means of soap solution or dissolved with very dilute hydrofluoric

acid before the final chromic acid treatment. The acid bichromate solution is drained out and thoroughly washed off with distilled water. If alcohol and ether are used to accelerate drying they must be freshly distilled and filtered: ether, in particular, is liable to leave an oily residue due to oxidation products if it has been stored long, and I prefer to avoid its use. The drainage of distilled water from a glass surface affords an excellent test of cleanness and is fairly rapid if the temperature is not too low. The subsequent drying requires the passage of a stream of filtered air through the instrument, which is gently warmed if the washing has been concluded with water.

Rubber tubing is generally employed for attaching to the viscometer either the tube supplying air for drying or the stop-cocks used in making the definitive connexions to the manometer and constant pressure apparatus. New rubber tubing is a fruitful source of trouble, and the French chalk or other powder with which it is frequently dusted should be removed by washing with soap and water or boiling with caustic soda. I prefer, however, to push the ends of the viscometer limbs through small bored rubber bungs before beginning the cleaning operations, so that these bungs may be left in position until perished: all connexions to the viscometer are then made by means of glass tubes of which the last few centimetres are expanded to suit the bungs. A ground glass joint in a similar position might be preferable. In any case the joint must be so made or so supported that there is no possibility of the viscometer being blown off when pressures are applied. The requisite degree of gas-tightness is easily attained.

The removal of suspended particles from liquids which are to be introduced into the viscometer may be effected, in the case of pure chemical individuals, by processes of distillation and filtration continued, if the liquid is transparent, until it appears optically void. Filter papers should be of hardened paper: if paper of a loose texture is used, interruption of the filtration is liable to cause the detachment of fibres. Filter-plates consisting of finely divided glass fritted together and fused into glass tubes are now available; these are free from many of the defects of paper and are very suitable for retaining fibres in the last stage of the purification, though their pores are not so fine as those obtainable with paper. Fritted glass (or quartz) filters may also be used with many solutions which attack paper or suffer preferential adsorption of one

of their constituents by cellulose. The particles not removable by such filtration as is allowed by the nature of the liquid under test will naturally settle so slowly that they may not be retained by dust-traps in the viscometer, and they may be carried through the capillary without causing obstruction. The observation made by many workers, that flow times are liable to increase when liquids are left in a viscometer over night, is usually attributed, in the absence of other assignable causes such as evaporation of solvent from a solution, to the deposition of suspended particles which tend to adhere to the capillary walls; such adherent particles may become detached during repetitions of an experiment.

The introduction of the (filtered) liquid into a viscometer of the Thorpe and Rodger type is effected by means of a siphon tube leading from the sample bottle to the bottom of the viscometer. The external diameter of the siphon being limited by the size of the constrictions in the vertical limbs of the viscometer, the filling operation may become tedious, and involve unduly long exposure of the liquid to air, unless pressure is applied above the surface of the liquid in the sample bottle. The application of suction in the transference of liquid into the viscometer and from one arm to the other is liable, in many cases, to give trouble owing to the disengagement of bubbles of dissolved air. The quantity of liquid to be introduced is a little more than the working volume at the lowest temperature at which tests are to be made. The adjustment of the working volume is made by means of the overflow traps after the temperature has been adjusted, and is repeated whenever observations are to be made at a different higher temperature.

The operations of cleaning and filling the viscometer are facilitated if a framework is provided to which the instrument may be clipped. The clip should be such as to ensure a reproducible position of the viscometer relative to the framework: the latter may then be fixed in a standard manner in the thermostat so that the hydrostatic head is constant from one experiment to another.

(B) *Making a measurement: temperature and timing.* The viscosity of water at 20° C. varies by 2·5 per cent. for a change in temperature of 1° C., while that of castor oil at the same temperature varies by 8·5 per cent. It is therefore impossible to determine the viscosity of water with an accuracy of 0·1 per cent. unless the temperature is constant and known to 0·04° C.: a similar

percentage accuracy in the case of castor oil would require that the temperature be known to 0·01° C. Although variations in temperature of a few thousandths of a degree are easily detectable with a suitably graduated thermometer, the value on the International Standard or constant-volume hydrogen scale will not be known to 0·04° C. when a mercury thermometer is used unless a recent comparison has been made with the standard thermometers maintained by the National Physical Laboratory at Teddington, the Bureau of Standards at Washington, or the corresponding institutions in other countries. Calibrated thermometers must of course be used under conditions similar to those prevailing during the calibration, if the corrections given are to be valid: certificates from the N.P.L., for example, hold for a rising meniscus and total immersion unless otherwise stated. Corrections are not stated to better than 0·01° C. except for thermometers having a very open and therefore restricted scale; hence using the most refined mercurial thermometry, viscosities in the neighbourhood of 10 poises could not be significant to 0·1 per cent even if the dimensions of the viscometer were known to a much higher accuracy. A recent exposition of the principles and practice of thermometry is given by Higgins.[58]

Since the temperature observed is that of the bath liquid rather than of the liquid in the viscometer, it is necessary that the viscometer be so immersed that the liquid in it never rises to within one or two centimetres of the outer level. Well stirred thermostats provided with suitable regulators can be readily maintained at temperatures constant to a few thousandths of a degree between 0° C. and 50° C. Regulation is particularly essential if the volume of the viscometer is large, so that equilibrium of temperature may be attained before the flow is begun. Unless stirring is vigorous, differences of temperature between the surface layers and the body of the bath liquid may be considerable, especially at temperatures far removed from that of the room: it is advisable to use a thermometer having a length such that, with the specified depth of immersion, its bulb may be close to the capillary of the viscometer.

When the filled viscometer has stood in the bath at the desired constant temperature for a time varying from about 10 minutes (for a 2 cm.³ bulb) to 30 minutes or more (for a 20 cm.³ bulb) the adjustment of the working volume is made by forcing the liquid

in the right arm slowly down to the mark 1 (Fig. 8), allowing the excess to overflow from the jet F. The stop-cocks are then turned so that the right-hand arm communicates with the air and the left-hand with the constant pressure supply, which has previously been regulated to the desired value. The manometer reading is taken before the meniscus of the liquid in the viscometer reaches the mark 3; the stop-watch is started as the meniscus passes this mark and stopped when the mark 2 is reached; the reading of the manometer is checked and the stop-cocks are turned so as to be ready for observation of the time of flow in the reverse direction.

Stop-watches should be used in a definite position, should be fully wound before starting each measurement and should be compared with a good clock or chronometer *regularly*. Inferior stop-watches sometimes gain during one part of the revolution of the seconds hand and lose in another part, so that they are in error at the 20 second mark and correct at the 60 second mark. I once had a watch of excellent pattern which after long use became liable to omit to record a minute after running about 5 minutes and then to continue as though it had behaved normally.

(C) *Calculation of the constants of the viscometer.* The measured volume of the bulb and length of the capillary are sufficient to enable us to calculate the approximate value of the constant K_1 of equation (III. 11) on the assumption that $m = 1 \cdot 10$. If we know the mean radius of the capillary tube (§ 2 A (3)–(5)), we may also find the constant K accurately assuming $n = 0 \cdot 85$ (see § 2 A (1)). When the times of flow of water have been noted for filling and for emptying the bulb at constant temperature with a given externally applied pressure p_0 (see § 2 B (2)), we have the data requisite for calculating the hydrostatic head according to equation (III. 12). The true value of the average effective pressure in any experiment is then deduced as in § 2 B (3), introducing a small logarithmic head correction if necessary. If the kinetic energy may become appreciable we proceed to find from any series of tests made with one and the same liquid at constant temperature, the values of m, possibly slightly different from each other and from $1 \cdot 10$, which are appropriate to flow in each direction through the capillary. For this purpose the graphical method of Knibbs (Chap. II § 6 a) may be adopted, but the possible variations of delivery volume of the bulb (§ 2 C (3)) must be taken into account,

by applying a correction to the assumed constant value of V, in analysing the observations for rate of emptying of the bulb. Further, unless a long interval has been allowed for drainage before reversing the flow, it may not always be legitimate to assume a negligible volume for the film which remains on the walls of the measuring bulb before the rising meniscus reaches it: the necessary correction might be determined during the construction of the viscometer, but it is a simple matter to observe whether the times of filling are actually independent of the time of previous drainage. With the highest rates of filling there might appear to be an increase in the value of m owing to an indirect effect of the retention of liquid on the walls of the right-hand bulb (Fig. 8): the level in this limb would then fall below the lower constriction $2'$ before the meniscus in the left-hand bulb reached the upper fiducial mark 3. The consequent reduction in the effective driving pressure and prolongation of the time of flow would cause the true value of the product Pt, corresponding with the abscissa $1/t$ given by the observed time of flow, to lie below that calculated on the assumption that the mean hydrostatic pressure remains constant for all rates of flow. The elimination of this error would be difficult, but fortunately it appears likely to be negligible except possibly for liquids considerably more viscous than water used in very long and narrow bulbs.

After amending, if necessary, the value first deduced for the mean hydrostatic head in the viscometer, by introducing more accurate estimations of m, the equations to be used in calculating viscosity from subsequent observations of pressure and time may be written, if $x_0\rho g$ is always less than $1/30$ of p_0,

$$\eta = K\left(p_0 \pm x_0\rho g\right)t - K_1\rho/t.$$

Here K is still subject (for flow from left to right) to the small variations found in the calibration of the bulb for delivery, and K_1 may require to have different values for the two directions of flow. The density ρ of the liquid at the temperature of experiment requires to be known, but only to 1 per cent. if the kinetic-energy term is not allowed to exceed 10 per cent. of the viscosity.

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COMMERCIAL ABSOLUTE VISCOMETERS

THE use of various forms of short-tube viscometer has been so general in certain industries, notably in that of petroleum, that some account of the instruments standardized in different countries must be included in any survey of viscometric practice. Many readers may be surprised to find these viscometers described as 'absolute', since much play has been made of the adjective in the course of diatribes on the demerits of instruments of this class as compared with those which have been used in physico-chemical research. The Redwood, Saybolt, and Engler viscometers, however, may lay claim to the description in that their standardization depends in the first place on dimensions, the calibration which has been found necessary to ensure uniformity being in the nature of a refinement due to the impossibility of specifying the dimensions to the precision required. The dimensions of the Barbey 'ixomètre' are less accurately defined and rather more scope is allowed for adjustments during manufacture, but it will be most appropriately included in this chapter.

The principle underlying the design and use of each of the first three of these viscometers is essentially the same. The liquid to be examined is poured into an open cup or tube mounted in a small bath which can be filled with water or oil to provide temperature control. In the middle of the base of the cup there is a carefully bored jet which is provided with a simple form of valve. The level of the liquid in the cup is adjusted to a definite height, the jet is opened and an observation is made of the time required for a stated volume to be discharged through the air into a measuring vessel placed below the jet. The British, American, and German viscometers differ in almost every detail, in the material, diameter and length of the outlet tube, in the shape of the cup and disposition of the bath, in the means adopted for defining the initial level and for plugging the jet, and in the volume discharged. The official descriptions may be found in the specifications set out in Appendix I, to which reference should be made in connexion with the following notes on the history and standardization of each viscometer.

A. The Redwood viscometers (p. 293).

Redwood No. I viscometer. The design of the No. I viscometer by Boverton Redwood[1] in 1885 was stated by him to be a modifica-

tion of an instrument devised by C. Rumble, chemist to Price's Patent Candle Company at Battersea. Redwood attached considerable importance on the score of permanence to the use of agate as a material for the jet, which was cemented into a slightly conical seating in the metal base of the cup. Small variations in the dimensions of the jets were compensated by adjustment of the height of the filling-point during the construction, so that a viscous oil might give the same time of flow in any instrument. In order that engineers using mineral oils in place of the older types of lubricant might appreciate the significance of the 'viscosity' as measured by this viscometer, Redwood expressed the viscosity as a percentage of that of rape oil at 60° F., the times of flow being regarded as proportional to the kinematic viscosities. He found that at this temperature the average time of flow of 50 cm.³ of rape oil from different sources was 535 seconds, but considerable deviations from this figure have been reported by later observers, and it eventually became the practice to state results in 'Redwood seconds', making no correction for variations in specific gravity.

Owing, presumably, to the difficulty of obtaining accurately bored agate jets, Redwood did not specify the exact bore but required the jet to be such that the time of flow of 50 cm.³ of rape oil at 60° F. could be made equal to 535 seconds by adjusting the filling-point to a height differing from the normal by not more than $\pm \frac{1}{4}$ inch. The specification prevailing from 1912 (or earlier) to 1924 is given in a paper by Higgins.[2] From the mention of the use of rape oil in fixing the tolerance on the bore it has been assumed that the calibration of the instrument depended on the admittedly variable viscosity of this product, but actually viscometers approved by Redwood were compared in his laboratory with his own standard apparatus by observation of the relative times of flow of either rape or a suitable mineral oil. The assumption is possibly responsible for the existence of a number of instruments which give flow times differing by as much as 8 per cent.; these can hardly have been calibrated by direct comparison.

Higgins's paper contains a discussion of the effect of errors of experiment on the results obtained. He states that the initial height of filling is reproducible to about 0·2 mm., corresponding with an error of 0·25 per cent. in time of flow, and that the small spirit-levels supplied are sensitive to about 1/5°, corresponding

with a maximum error of 0·1 per cent. From the comparisons of the 'Redwood times' of eight oils at temperatures from 10° C. to 60° C. with the viscosities measured in a carefully calibrated apparatus of the Thorpe and Rodger type, he arrived at the following formula:

$$\eta/\rho = AT_R - B/T_R, \text{ with } A = 0\cdot00260 \text{ and } B = 1\cdot715. \quad \text{(IV. 1)}$$

This conversion equation gives the value of the viscosity in poises corresponding with any Redwood time T_R secs. (greater than 34 seconds), when the density in gm. per cm.³ at the temperature of an experiment is known. In a critique of Higgins's equation I have shown[3] that the data given in his tables should probably be interpreted as leading to a value $A = 0\cdot00255$ for the instrument used by him.

Herschel[4] examined two Redwood instruments, using the method described in Chap. II, § 6 (c), to evaluate the Couette and kinetic-energy corrections: introducing these results and the dimensions of the apparatus into the Poiseuille equation, he obtained for one viscometer $A = 0\cdot00259$, $B = 1\cdot905$. Since this instrument had a jet 0·985 cm. in length and B is equal to $mV/8\pi(l+na)$, he proposes to reduce his value of B to 1·88 to make it applicable to a jet of standard length. A second instrument having a jet only 0·964 cm. long gave a negative Couette correction, owing presumably to irregularity of the bore; the results obtained with this apparatus, which appear to lead to a value for A about 0·00266, were therefore neglected in the final equation.

In 1924 the Institution of Petroleum Technologists issued in its *Standard Methods of testing Petroleum and its Products* an official specification for the construction and method of use of the Redwood viscometer. Since that time the testing of new instruments has been carried out at the National Physical Laboratory, which has furnished reports on dimensions and on times of flow as compared with the instrument (No. 1307) used in Higgins's experiments. It was found that the diameter then specified for the jet (1·59 mm.) was inconsistent with the requirements of a cylindrical bore giving a flow time agreeing with No. 1307: pending revision, the operation of the clause stating the diameter was suspended.

The routine measurements of viscometer dimensions and comparisons of the times of flow of an oil having a 'viscosity' of some 350 Redwood seconds through various instruments have brought

to light some facts which should be recorded. By the use of a series of gauges, made by holding the ends of thin rods of enamel glass in a flame until a nearly spherical bead was produced, it has been found possible to examine the shape of the bore of the agate jets and to obtain measurements of diameter at various positions. By the courtesy of Mr. Robert Redwood the original viscometer used by Sir Boverton Redwood was lent to the Laboratory for a few days, during which it was ascertained that No. 1307 gave times of flow agreeing with this instrument within 0·9 sec. at 330 seconds and within 0·1 sec. at 94 seconds. The essential dimensions were compared, with the following results (expressed in mm.):

Instrument.	*B.R.*	*No.* 1307.
Diameter of oil-cup	46·6	46·5
Height of filling-point above top of jet .	82·6	79·4
Length of jet	11·29	10·24
Internal diameter of jet minimum .	1·63	1·59
„ „ maximum .	1·66	1·67

The minimum diameter is in both cases near the middle of the jet. It will be observed that neither instrument is in accord with the present specification. It is possible, albeit rarely, to obtain agate jets of which the bore varies by less than 0·01 mm. from one end to the other. The position of the section of minimum diameter appears to affect the resistance of the jet, but the data are not sufficient to enable generalizations to be made. Some of the older jets, such as that of No. 1307, were very poorly polished, and the small minimum diameters were due to the agate being drilled from two ends along different axes. Rough places are particularly objectionable in practice owing to the difficulty of cleaning the jet and to the probability of suspended matter in the oil being retained on the walls. Flaring of the bore at the ends to the extent of a few hundredths of a mm. is not objectionable and is preferable to the occurrence of small chips, a defect which is particularly frequent at the exit end. In a few of the jets examined a flat has been ground on the convex base of the jet, presumably to avoid or to remedy chipping: to this again no exception need be taken if the flat does not extend more than 2 to 3 mm. from the bore.

If a jet of the specified length departs at all widely from the cylindrical shape, it is obvious that the correct resistance to flow

can be obtained only by reducing the bore at some point below
that of the equivalent cylinder. Such reduction increases the
probability of clogging and appears likely to affect the coefficient
of the kinetic-energy term and the value of the critical velocity
for the beginning of turbulent flow. In the revision of the speci-
fication by the Institution of Petroleum Technologists it has there-
fore been decided to specify a minimum diameter of 1·620 mm.;
in conjunction with the other requirements this should ensure a
close approximation to the desired cylindrical form without neces-
sitating any equipment more elaborate than a 'go' plug-gauge for
checking the shape.

For cleaning the jet after washing out with solvent it has been
found that twisted strips of tissue paper of good quality, or lengths
of the silk sold as 'dental floss', are suitable. Twine should not
be used, for if it is soft it is liable to leave loose fibres in the bore,
and if it is hard and polished there is some danger of wearing
the agate.

When two viscometers are to be compared, tests are made with
an oil having a flow time of some 350 seconds at approximately
room temperature; in the morning the baths are heated about half
a degree above the temperature prevailing when the filtered oil is
introduced, so that at the end of 20 minutes or so the stirred oil
and water are both very nearly in equilibrium with the now
warmer air. The flow times are then taken if the difference of
temperature between the oil in the two cups does not exceed
0·1° C.; a correction is applied for any small difference in mean
temperature. This procedure avoids the differences in temperature
gradient which are inseparable from any attempts to adjust the
two temperatures to equality by heating or cooling during or
immediately before the flow; it is possible, with practice, to repro-
duce the ratios of times with a consistency of 0·2 per cent. or
better.

In determining the time of flow of an oil through a viscometer
at a specified temperature considerably different from that of the
air, the most accurate results are obtained, not by repeated rapid
adjustments of temperature whenever the thermometer indicates
a departure from the desired condition, but by setting the heating
flame to a height such that the rate of heating or cooling is very
slow, and leaving it untouched during and for several minutes
prior to the test. If the first observation has been made when the

temperature is rising, the duplicate test should be made when it is falling. Assuming that the rates of change are small and equal and that the mean temperatures during the flow are identical, the average of the two times gives an accurate value for the time at this mean temperature. The times will naturally differ more than if the temperatures had been varying in the same sense, but their average will be more independent of the lag. Instead of waiting until the exact temperature specified is reached, it is usually more expeditious to apply corrections for small departures therefrom; the temperature coefficient may either be directly measured or may be inferred with sufficient accuracy from the actual viscosity if the correction is small and the product is of a known type.

The directions for use given by the Institution of Petroleum Technologists recommend that the recipient flask be thermally insulated when tests are being made at high temperatures. Any formula for the conversion of times of flow into kinematic viscosities assumes that the liquid is measured at the same temperature as that prevailing in the cup and jet. Since oils contract by about 0·065 per cent. per 1° C., the insulation suggested is normally adequate for the accuracy attainable in routine work: for very viscous oils at high temperatures a correction may be made for the cooling error by taking the temperature of the oil in the flask after stirring at the end of the run and making use of the above coefficient of expansion. In any case no very great accuracy is to be expected at high temperatures, since the instrument was not designed for such tests.

The revision of the specification for the Redwood viscometer has only recently been published.[5] Since the bore of the jet is now fairly definitely laid down and certain minor defects of the original specification have been remedied, it will be possible for the National Physical Laboratory to issue certificates for instruments complying with the requirements. It has been found that there is some liability to variation in the value of B in the equation for these viscometers: hence the certificates will state the extent of divergence from the standard instrument for flow times in the neighbourhood of 60 seconds. A redetermination of the constants of the equation for conversion of Redwood times to kinematic viscosities is to be made, when an opportunity occurs, using an instrument having a jet with nearly cylindrical bore and conforming in all details with the new specification.

Redwood No. II Viscometer. The Redwood No. II viscometer was originally designed by Sir Boverton in connexion with investigations on oil fuel which he was making for the Admiralty, and the design was registered as 'Admiralty type' by the manufacturers of his apparatus, Messrs. Baird & Tatlock (London), Ltd.: since the publication of a specification by the Institution of Petroleum Technologists other makers have produced similar instruments. Oils for which the No. II viscometer is suitable ($\eta > 5$ poises) have high temperature coefficients of viscosity and are very liable to exhibit the phenomena of hysteresis and of variation of viscosity with rate of shear (see Chap. XI). Hysteresis effects may be made fairly reproducible by the procedure laid down in the specification, but the standardization in absolute units of viscometers of high range requires the use of liquids having normal behaviour. By using castor oil for the intercomparison of No. I and No. II viscometers one may apparently be sure of obtaining the true relation between the instruments, but unusual precautions are necessary to avoid errors due to differences of temperature. Owing to the difficulty of standardization no authoritative conversion formula for the No. II viscometer has been issued. On the basis of a few measurements with fuel oils, some of which were found to show hysteresis effects which had not previously been suspected, Pannell and Higgins[6] adopted a tentative equation similar to (IV. 1) in which the values of the two constants, after conversion into the C.G.S. system, become $A = 0.0270$ and $B = 12.0$.

Later comparison of their instrument with a No. I viscometer, using castor oil in both, has shown that the value of A is almost exactly ten times that for No. 1307. Substitution of $L = 5$ cm. in the expression $B = mV/8\pi L$ gives $B = 0.40$ as a value which should be approximately correct for the coefficient of the term involving $1/T$. If B is as low as is here suggested, it should be possible to use this instrument without important error in the examination of oils having viscosities as low as 0.5 poise, for which the 'Redwood No. I' time is nearly 200 seconds. Preliminary comparisons appear to confirm this deduction, the errors being no greater than those due to the decreased accuracy of timing.

Liquids for which the Redwood No. II viscometer is specified, giving times of flow above 2,000 seconds in No. I, are difficult to free from suspended impurities: further, the apparatus is actually used in many cases when there is no certainty that the rate of

shear will not affect the apparent viscosity. Hence it becomes important that the minimum diameters of the jets of different viscometers shall agree as closely as possible. The minimum which has now been fixed (3·80 mm.) is sufficiently high to ensure also that the jets shall not depart far from the form of a right circular cylinder.

B. The Saybolt viscometers. An early form of this visco-meter, designed by G. M. Saybolt of the Standard Oil Co. of New York, was exhibited by Redwood during the discourse[7] in which he gave the first description of his own instrument. The original apparatus differed from that now specified (Appendix I) in some minor points such as the use of a row of small holes in the wall of the oil-cup, instead of an overflow rim, to define the initial level of the oil. A difference of principle lay in the fact that the volume of efflux was measured in the oil-cup itself: in order that the final level might be observed, the cup was joined to the jet by means of a narrower tube which was lined with glass and cut away near the mark. Not only did this extension of the cup render cleaning more difficult and increase the working head, but it necessitated the provision of windows in the bath and made the apparatus more cumbersome. Saybolt viscometers more similar to the present form were described and examined by Meissner[8] and by Herschel,[9] but the conversion equations obtained with these instruments were rendered obsolete by the subsequent standardization of dimensions agreed between Mr. Saybolt and the Bureau of Standards, and eventually adopted by the American Society for Testing Materials, for the Standard Saybolt Universal Viscosimeter.

Herschel[10] observed the times of discharge of a series of liquids of known kinematic viscosity through four Saybolt Universal instruments of which the dimensions approximated to those now specified as normal. Applying the methods described in Chap. II, § 6 (c), to the analysis of his results, he obtained as the equation for conversion of 'Saybolt Universal seconds' T_{SU} to viscosity

$$\eta/\rho = A T_{SU} - B/T_{SU} \qquad [A = 0 \cdot 00220, \ B = 1 \cdot 80]. \ \text{(IV. 2)}$$

Saybolt Universal viscometers are tested at the Bureau of Standards and, if the dimensions are found to lie within the limits allowed by the specification, a comparison of flow time is made against a standard or master tube and a certificate giving correc-

tions is issued. One oil only is used in this comparison (S.U. time ca. 180 sec. at 100° F.) and it is assumed that the specification of dimensions is sufficient to ensure that B has the value found for the Bureau instrument. As a result of more detailed examination of the master tube held by the Bureau of Standards, Herschel has decided that an equation of the above form with $A = 0.00226$ and $B = 1.9$ holds for this instrument up to $T_{SU} = 125$ sec. only, and that above $T_{SU} = 200$ sec. the equation becomes

$$\eta/\rho = C T_{SU} \qquad . \qquad . \qquad . \qquad . \text{(IV. 2 a)}$$

with $C = 0.00220$. A table embodying these more recent results and giving the kinematic viscosities corresponding with various efflux times observed on the master instrument is reproduced in *International Critical Tables*, vol. i.

In the same volume is given a similar table for the conversion of 'Saybolt Furol seconds' to kinematic viscosities. No description of the calibration of the Furol instrument appears to have been published, but the two conversion equations are stated by Herschel to be

for $25 < T_{SF} < 40$,

$$\eta/\rho = A T_{SF} - B/T_{SF} \ldots [A = 0.0224, B = 1.9], \quad . \text{(IV. 3)}$$

and for $T_{SF} > 80$, $\qquad \eta/\rho = C T_{SF} \ldots [C = 0.0216] \quad . \quad \text{(IV. 3 a)}$

Herschel has described[11] a modification of the Saybolt viscometer, called the U and F viscometer, in which jets having the dimensions required for the Universal and for the Furol viscometers may be substituted for one another. The dimensions conform to those normally specified except that the cup is made a little wider to allow the thermometer to be left in position throughout the test (see next paragraph).

Not only is the oil-cup of the Saybolt instrument better adapted by its shape than is that either of the Redwood or of the Engler viscometer to a rapid equalization of temperature between the liquids inside and outside the cup, but the bottom of the outlet tube is about 1 cm. above the bottom of the bath, giving some measure of control over the temperature of the liquid in the jet. The latter feature appears in the Redwood No. II instrument, but not in the Redwood No. I or in the Engler. In spite of the narrowness of the oil-cup it is found necessary to maintain the bath somewhat above the temperature required for the oil (e.g. at

212° F. for a test at 210° F.) in order that the average temperature of the oil during a run may approximate to that desired. Herschel[11] has examined the error produced by the variation of the temperature of the oil in the jet from that of the oil in the cup. He found, for example, on making tests with an oil having a time of discharge of 200 seconds at a nominal temperature of 100° F., secured by maintaining the bath at 100·25° F. when the room temperature was 77° F., that the kinematic viscosity deduced from the above equation was 2 per cent. greater than the true value. He suggests that the true kinematic viscosity ν at the nominal temperature of test θ, may be found from an equation of the form

$$\nu = (AT - B/T)\left[1 - \frac{1}{\nu} \cdot \frac{d\nu}{d\theta}\{\theta - \theta_m + c\,(\theta - \theta_r)\}\right], \quad \text{(IV. 4)}$$

in which θ_m is the average temperature of the oil in the cup during the run, θ_r is the room temperature, and c a factor which is probably an approximate constant. In order to obtain θ_m it is necessary to leave a thermometer in the oil throughout the test, a procedure which entails a decrease of the mean head and divergence from the standard Saybolt time unless the oil-cup is made correspondingly wider as in his U and F modification.

C. The Engler viscometer. The viscometer which bears the name of Engler was the first to receive official recognition, having been adopted for use by a German railway committee as early as 1884. The original form of it was described by Engler in 1885,[12] but after complaints had arisen of discrepancies between the results given by instruments obtained from different makers, he gave a more detailed account of a slightly improved pattern.[13] The manufacture of this pattern was then restricted to one maker, Desaga of Heidelberg, and approved instruments were stamped by the Prüfungs- und Versuchsanstalt of Karlsruhe. In 1907 this institution, the Physikalisch-technische Reichsanstalt of Charlottenberg and the Materialprüfungsamt of Gross-Lichterfelde-West, issued the specification of dimensions which is reproduced in Appendix I. The three upturned points m (Fig. 53) serve not only to fix the initial height of the liquid but also to level the apparatus. In the original instructions the 240 cm.³ required to fill the cup to the correct height were measured out in a graduated flask marked at 200 cm.³ and at 240 cm.³, and the flask was merely drained for one minute before being placed under the outlet. The

flask was calibrated for delivery (presumably of water), but it was
pointed out by Holde[14] that this procedure involved error. Erk[15]
showed that the volume left in the flask after one minute's draining
amounted to some 10 cm.[3] ($= 5$ per cent.) with an oil having
$\nu = 9 \cdot 2$ cm.[2]/sec., and varied with the shape of the flask. Holde
and Erk therefore recommended that the flasks be calibrated for
content and cleaned before use; this is of course normally done in
the case of the 50 ml. and 60 cc. flasks of the Redwood and Say-
bolt viscometers. The objection, however, appears to be mainly
academic, since in practice the error would be constant for a given
oil except when flasks of very different form were used.

The shallow oil-cup of the Engler instrument entails an appre-
ciable gradient of temperature in the oil when tests are made above
room temperature. At 50° C. it is necessary to keep the bath 1° to
1·5° C. warmer than the oil, and considerable time may be required
before the stirred oil comes to rest. The observation of the time
of efflux of 200 cm.[3] of water at 20° C., on which the calculation of
'Engler degrees' is based, is of some value in enabling the occur-
rence of accidental damage to or obstruction of the jet to be
detected, but it is evident that the change in time of efflux of an
oil will not be proportional to the change in 'water value'. The
determination of water values is probably a more accurate check
on the dimensions of the jet than can be secured by specification
of the bore, but it does not allow the constant A of equations such
as (IV. 1) or (IV. 2) to be fixed with anything like the same pre-
cision as is afforded by direct comparison with a standard instru-
ment by tests with a viscous oil.

The above defects in the construction and method of calibration
of the Engler viscometer are quite sufficient to account for the
large differences between the formulae which have been suggested
by various workers for the conversion of the results obtained to
absolute units. The equation which has been most widely used,
in spite of many adverse comments, is that due to Ubbelohde
which forms the basis of a book of tables[16] issued by him in 1907;
it may be written

$$\eta/\rho = 0 \cdot 073 \, E - 0 \cdot 0631/E, \quad . \quad . \quad . \quad (IV. 5)$$

where $E =$ Engler degree $=$ time of flow of 200 cm.[3] divided by
the water value. Erk[15] compares this and some of the other pro-
posed formulae with the results of his own experiments, and finds
that the best agreement is obtained with an equation put forward

by Vogel.[17] The full formula contains an undetermined correction applicable to tests at elevated temperatures; neglecting this correction, Vogel's formula may be written

$$\eta/\rho = E \times (0\cdot0760)^{(1-1/E^3)}. \qquad . \quad . \quad . \quad \text{(IV. 6)}$$

A table based on this equation is given in an Appendix to Erk's paper. Tables for the conversion of 'Engler seconds' to Saybolt or Redwood times or to kinematic viscosities have been prepared by different workers. Although the times of flow of a given oil in different Engler instruments are more variable than the 'Engler degrees', such tables are of use in facilitating the comparison of tests made in the three types of viscometer; they should be based, however, on an assumed 'water value' of 51 seconds, which is the normal from which divergences of 2 per cent. are allowed, rather than on the actual 'water value' of any one instrument.

For a description of modifications of the Engler viscometer by Kunkler and by Martens, and of a number of other viscometers now obsolete, see Redwood.[18] The Lamansky-Nobel apparatus there mentioned is more fully described by Holde[19]: Holde states that this is still used in Russia and that the factor for conversion of Lamansky-Nobel viscosities (which are relative to water at 50° C.) to Engler degrees varies from 1·13 to 1·26.

The formation of drops.

In the use of the three technical viscometers above described it is observed that the flow of the more viscous oils differs from that of mobile liquids in that the discharge occurs, not in a continuous stream, but in a series of drops. Particularly in the Redwood and Saybolt instruments it may be remarked that over a certain range of viscosities the discharge begins by being uninterrupted and breaks up into drops towards the end of the run when the head has become considerably reduced. The transition suggests the possibility of a break in the curve connecting viscosity with time of discharge, but none of the published curves exhibits any signs of a change in slope at the critical viscosity. From an approximate analysis of the conditions prevailing during the formation of drops at the outlet of the Engler jet, using Lohnstein's table to find the ratio of the weight of a falling to that of a pendent drop of oil, Erk[20] arrives at an estimate of 0·7 mm. as the average reduction of the driving head by forces due to surface tension. Since this reduction is only some 2 per cent. of the mean hydrostatic head,

which is 39·6 mm. according to Meissner,[21] it is not surprising that
it should escape recognition in the calibration of such viscometers,
especially in view of the fact, above indicated, that the transition
occurs over a range of viscosities.

D. Barbey's 'ixomètre'. Although it is little known outside
France and is by no means exclusively
used in that country, this instrument
possesses certain features which render
it of interest from both the practical and
the theoretical aspects. It was invented
by L. Barbey, of the Laboratory of the
Compagnie de l'Est, with the objects of
minimizing cooling of the liquid in the
jet and of decreasing the risk of obstruc-
tion. The first account of the apparatus
was given in an appendix to a paper by
Salomon[22]; a m.... le déposé is supplied
by MM. la Société des usines chimiques
Rhône-Poulenc of Paris, of which the
following is a brief description (see Figs.
15 A and B).

At the top of a vertical tube B (13
mm. diameter) is fitted a funnel F
provided with an overflow P; the liquid
to be examined is normally contained in
a glass separating funnel L, the tap of
which is so adjusted, after the remain-
der of the apparatus has been filled,

Fig. 15 A. Barbey's 'ixomètre',
explanatory diagram.

that a slow stream drips from P into a beaker M. The vertical
tube B is connected at its lower end, by means of a horizontal
tube of 8 mm. bore, with a rising vertical tube D of 5 mm. bore,
in the axis of which lies a steel rod E of 4 mm. diameter,
centred by a depression in a cap O closing the bottom, and by
a hole in another cap N closing the top of D. Near the upper
cap N is a spout G serving to fix the outlet level and to lead the
liquid to a graduated receiver K. When the system has been
filled with liquid, air-bubbles being excluded by the adoption of
suitable precautions, the bath is placed in position and the tem-
perature regulated. Under the constant head represented by the

vertical distance between the overflows at P and G, the liquid streams at a constant rate through the annular channel, about 20 cm. long, between the rod E and the tube D; it may be noted that this 'jet' is immersed in the bath except for a fraction of its length. The volume collected in K during 10 minutes is read after warming it to the bath temperature. The unit of the graduations is one-sixth of a cm.³, so that the reading gives the number of cm.³ discharged per hour, which is called the 'Barbey fluidity'. Four receivers having capacities of 30, 60, 90, and 120 cm.³ allow tests to be made, with the normal 10 minutes of discharge, on oils of widely different fluidity. For tests at high temperatures it is recommended that L be made of metal so that the oil may be kept warm by a flame.

The original adjustment of the apparatus is such that refined rape oil at 35° C. gives a Barbey fluidity of 100. The makers supply a standardized mineral oil by the use of which an observer may detect the development of any change in the constant of the instrument owing e.g. to corrosion or wear of the rod E.

FIG. 15 B.   Barbey's 'ixomètre', (MM. Rhône-Poulenc).

The Barbey instrument is unique in that it is the only practical viscometer in which use is made of a flow-tube of annular cross-section. In calculating the distribution of velocities for such a section by the method indicated in Chap. II, § 3, the coefficient of the logarithmic term on the right of equation (II. 2) is not zero, but there is a second boundary condition, viz. $u = 0$ for $r = b$, where b is the radius of the inner circle. The equation for the velocity at any point in an annular pipe is given by Brillouin,[23] who shows also that the rate of discharge is

$$Q = \frac{\pi P}{8 \eta l}(a^2 - b^2)\left\{a^2 + b^2 - \frac{a^2 - b^2}{\log_e a/b}\right\} . \quad . \quad \text{(IV. 7)}$$

When $(a - b)$ is a small fraction of b, the two bracketed terms of

this equation, which replace the a^4 of the equation (II. 3) for a circular section, reduce approximately to

$$\tfrac{1}{2}(a^2-b^2)(a-b)^2. \qquad . \qquad . \qquad . \qquad \text{(IV. 7 a)}$$

Since the cube of the clearance between the inner and outer walls enters into the approximate expression for the rate of discharge under a given head, it is obvious that the occurrence of any eccentricity will be of importance. A calculation is given by the Editor of *Engineering*[24] for the extreme case in which the core actually touches the wall: his approximate solution indicates that under such conditions the volume discharged per second becomes $2\tfrac{1}{2}$ times as great as that through a concentric annular pipe. Experiments on the transition from stream-line to turbulent flow in the channel between co-axial pipes are recorded by Lonsdale.[25]

The deduction of a kinetic-energy correction term to equation (IV. 7) by a method similar to that explained in Chap. II, § 4, is somewhat tedious. It is obvious, however, that the coefficient m of this term will be intermediate between that found for flow in a circular cylindrical tube and that for flow between parallel planes. The first approximation obtained in equation (II. 4) for a circular section gives $m = 1$; it may be shown that the corresponding approximation for parallel planes (cf. Chap. VI) is $m = 27/35$. In view of the effect of the conditions at the entrance (cf. Chap. II, § 4) it will be sufficiently accurate for our present purpose to assume $m = 1$. We may write a corrected equation analogous to (II. 7 a) in the form

$$\eta = \frac{\pi h \rho g l}{8\,Vl}[R]^4 - \frac{m\rho V}{8\pi t l}\frac{[R]^4}{(a^2-b^2)^2}, \qquad . \qquad . \qquad \text{(IV. 8)}$$

where
$$[R]^4 = (a^2-b^2)\left\{a^2+b^2 - \frac{a^2-b^2}{\log a/b}\right\}.$$

For a given instrument in which a, b, and h are fixed, and with a constant time of collection of the effluent oil, this equation may be simplified to

$$\eta/\rho = \frac{A}{V} - BV. \qquad . \qquad . \qquad . \qquad \text{(IV. 8 a)}$$

If $t = 3{,}600$ secs. the volume V which would be collected in that time is the 'Barbey fluidity'.

If the dimensions were known with sufficient accuracy it would be possible to calculate the values of A and B in equation (IV. 8 a). We may obtain an estimate of the value of B by assuming $a = 0.25$

and $b = 0.20$; the approximation (IV. 7 a) for $[R]^4$ then gives $B = 3.1 \times 10^{-8}$, a value which will vary only with the first power of the difference of radii. If $A = 48.5$, the kinetic-energy term will thus amount to not more than 1 per cent. when the kinematic viscosity is 1·2 times that of water at 20° C. For practical purposes the term may be considered negligible and the equation becomes simply

$$\eta/\rho = A/V. \quad . \quad . \quad . \quad . \quad \text{(IV. 8 b)}$$

The diameters of the rod E and efflux tube D vary considerably, in some instruments, from those given in the above description of the ixomètre, and the reproducibility of the constant A depends on the adjustment of effective head by the makers. A comparison of a Barbey with an Engler instrument by Pellet[26] indicated $A = 53$ for the normal temperature of 35° C.; the constant increased, however, at higher temperatures, especially in tests on oils of low viscosity. Nicolardot and Baume[27] used a calibrated Ostwald viscometer to determine the relation between Barbey fluidities and kinematic viscosities, and found $A = 48.5$ at 35° C.; in tests made between 0° C. and 35° C. with oils of viscosity up to 4 poises, discrepancies of ± 8 per cent. were observed. The makers, MM. Rhône-Poulenc, inform me that the value $A = 48.5$ was first established by Barbey himself in 1901; this factor appears to be generally accepted in France.* It is admitted, however, that when tests are made on liquids of low viscosity at high temperatures, the liquid may not have time to attain the bath temperature before it reaches the annular channel; this defect is tacitly recognized in the instructions for use, which recommend that the liquid should be heated before introduction. At very low temperatures, on the other hand, viscous oils may be somewhat warmed in the upper part of the efflux pipe which is outside the bath; this would lead to the fluidity observed being higher than the true value.

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* M. Henri Weiss of Strasbourg University informs me that unpublished preliminary work under his direction at the *École Nationale Supérieure du Pétrole et des combustibles Liquides* confirms the substantial accuracy of the constant 48·5 for the apparatus in that institution at temperatures below 35° C. I think that the very large divergences found by Dupouy[23] at temperatures much above 35° C. are probably due chiefly to errors of temperature in the apparatus used by him for absolute determinations, since the temperature-coefficients deduced from his measurements are too low. The relation given by Herschel[29], which leads to $A = 58$, is presumably based on the examination of an instrument which had not been satisfactorily adjusted.

Both errors tend to indicate unduly low temperature-coefficients of viscosity.

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CAPILLARY VISCOMETERS FOR RELATIVE MEASUREMENTS

IF liquids of known viscosity are available for calibration purposes there is no advantage to be gained by the use in routine work of viscometers which have been specially designed to comply with the requirements indicated in Chapter III as necessary for the accurate determination of viscosity in absolute units. On the contrary, the small diameters which have been shown to be essential for such instruments entail liability to obstruction which can only be obviated by the most elaborate precautions. Further, the viscometers discussed below can be made more compact and more robust than those described as suitable for absolute measurements, and the thermostats required are more conveniently maintained at constant temperature. On the score of accuracy, it has been argued by many workers, e.g. by Applebey,[1] that whereas determinations of the absolute viscosity of water by careful experimenters may show divergences of 0·3 to 1·0 per cent., it is possible to obtain the ratio of the viscosity of aqueous salt solutions to that of water with a precision of 0·01 per cent. The greater precision of the relative measurements is due partly to the simplification of apparatus and of procedure and partly to the avoidance of errors incidental to the measurement of dimensions.

'Relative' viscometers may be divided into two classes according as they are adapted for use with an externally applied pressure or rely solely on the hydrostatic head of the liquid in the viscometer for the production of flow. The advantage claimed for the former type is that with a single instrument it is possible to make tests on liquids of very widely different viscosity without inordinately prolonging the time of flow of the more viscous liquids. Taking 50 cm. of water as the lowest pressure which can be read with the required accuracy, in view of the necessity of making the logarithmic head correction negligible (cf. Chap. III, § 2 B (3 b)), the extension of range due to the adoption of this type of viscometer is fixed by the maximum head with which it is convenient to work. Assuming that rubber tubing is used for connexions, excess pressures of more than 500 cm. of water may be barred; for a given maximum time of flow, increase of pressure will therefore allow liquids to be tested which are ten times as viscous as those which

can be used in viscometers to which no external pressures are applied. Again, with the 'gravity' type it is necessary, in order to calculate the relative viscosity, to determine the density of the liquid under examination with a percentage accuracy higher than the accuracy of measurement of time of flow; with the 'pressure' type, the hydrostatic head of the liquid in the viscometer appears only as a correction term, and the density need not be known with any great precision.

Against the above-mentioned advantages of the pressure type of relative viscometer must be set the following disadvantages: (1) The necessity for the provision of a source of constant pressure and of gas-tight connexions therefrom to the viscometer and to a manometer. (2) The possibility of error either in the observation of manometric pressure or in the application of the various corrections required to find the effective driving pressure. (3) The fact that, owing to the magnitude of the pressure difference between the two arms of the viscometer, the capillary must be of smaller diameter than is necessary in a gravity-type viscometer to reduce the kinetic-energy correction to a specified limit. Although the permissible bore of the capillary varies only with the fourth root of the reciprocal of the driving pressure, I regard (3) as important, since the liability to obstruction increases very rapidly as the bore is reduced: such obstructions are the chief source of lack of concordance between duplicate experiments and are not always avoidable in routine work.

Fig. 16. Ubbelohde's viscometer (from Hatschek, *The Viscosity of Liquids*).

A. Viscometers for relative measurements using externally applied pressures.

1. General form. Apparatus similar to that of Poiseuille (Fig. 1) was employed by Graham[2] for experiments on the relative viscosity of several aqueous solutions, the ratio of the times of flow being measured with much greater accuracy than the diameter of the capillary. One of his viscometers, used in the examination of acid and alcohol solutions, had a bulb of 8·1 cm.[3], blown in

tubing of 2 mm. bore, sealed to a horizontal capillary of length 28 mm. and bore 0·094 mm.: with an applied pressure of 760 mm. of mercury this gave a time of flow of 348 secs. for water at 20° C.

Instead of allowing the liquid to be discharged into the bath, Pribram and Handl [3] provided similar graduated tubes at each end of the capillary, so that at the conclusion of a run the liquid could be forced back again for a second observation of time of flow. In their first apparatus the graduated tubes, of 2 mm. diameter, lay along prolongations of the axis of the horizontal capillary; the lack of precision in the reading of the positions of the meniscus in this arrangement led them to redesign the apparatus so that the graduated tubes were vertical, the capillary being bent twice at right angles to bring the limbs of the U-tube close together. To this bending of the capillary there are objections which will be discussed later (§ C, 4). They used a constant pressure of 1 metre of water, obtained by allowing water from a Mariotte bottle to overflow from a tube bent upwards inside an air reservoir. The capillary had a bore of 0·1 mm. and a length of 20 cm., and the apparatus was calibrated by means of water.

A much more satisfactory type of 'relative' viscometer was designed by Ubbelohde,[4] after the requirements of precise viscometry had been elucidated by the development of several of the absolute instruments described in Chapter III. Ubbelohde used his viscometer in the calibration of the Engler apparatus.[5] The method of measurement is sufficiently clear from Fig. 16 and the instructions given below for Bingham and Jackson's form.

FIG. 17.
Bingham and Jackson's viscometer (after Bingham, *Fluidity and Plasticity*).

In an investigation of the viscosity of sucrose solutions suitable for the standardization of technical viscometers, Bingham and Jackson[6] describe a compact form of relative viscometer (Fig. 17) embodying many of the features of Bingham's absolute instrument. The construction and disposition of the bulbs to reduce drainage errors and hydrostatic-head corrections are similar to those shown in Fig. 8, and the same overflow method of adjusting the working volume is used, a fiducial mark being so placed at H that the meniscus in the right limb is at the bottom or the top of

the double-cone shaped bulb on this side when that on the left
limb is at B or D respectively. The capillary is not attached by
ground joints but is sealed to the remainder of the apparatus: the
authors lay considerable emphasis on the necessity of using a
capillary with square-cut ends, sealed by their rims to the wider
tubing above and below. With this construction they consider it
safe to assume that the coefficient m of the kinetic-energy correc-
tion term has the value 1·12. In an appendix to his *Fluidity and
Plasticity*, Bingham adds the very necessary condition that the
second term of equation (V. 1) below should never exceed 5 per
cent. of the first, if any accuracy of 0·1 per cent. is desired. The
viscosity is to be calculated from the equation

$$\eta = CPt - C^1\rho/t, \quad \ldots \quad \ldots \quad \text{(V. 1)}$$

and C^1 is obtained (accurate to 2 per cent.) by substituting the
approximately measured dimensions of the instrument in the
relation

$$C^1 = 1·12\, V/8\pi l.$$

The value of C is found by making flow tests with a liquid of
known viscosity η_s, usually water: if the time of flow of the cali-
brating liquid of density ρ_s be t_s when a pressure P_s is applied, then

$$C = \frac{\eta_s + C^1\rho_s/t_s}{P_s t_s}.$$

In determining P or P_s the corrections to the manometer reading
which are detailed in Chapter III, § 2 B (2) and (3) must be
applied: the hydrostatic head is determined, as in the absolute
method, from flow tests in both directions. For the same reasons
as have been advanced in Chapter III, § 2 C (3) it is desirable, in
precise work, that the variations in volume delivered from the
bulb at different rates of discharge should be determined before
the viscometer is assembled; a drainage correction may then be
applied to results obtained with very viscous liquids.

2. Dimensions. In an appendix to his book, Bingham gives
detailed instructions for the design of viscometers of this type. He
appears to recommend the use of two instruments only, one suit-
able for use with liquids having viscosities as low as 0·2 cp. and
another restricted to viscosities above 2 cp. Making the assump-
tions that the minimum pressure to be read shall be 50 gm./cm.²,
that the volume of flow shall be 4 ml. and that the length of the

capillary shall be not greater than 20 cm., he gives tables showing that for the former instrument the radius of the tube should lie between 0·10 and 0·15 mm. and for the latter between 0·20 and 0·26 mm.: the lengths necessary to make the minimum time of flow equal to 200 secs., when radii between these limits have been selected, vary between 5 cm. and 20 cm. Although the criterion suggested at the beginning of the appendix is that the kinetic-energy correction shall not exceed 5 per cent., these limits are deduced by assuming $l/a > 500$ or 400, i.e. are such as to make the Couette correction negligible. Now the uncertainty in the latter correction does not affect determinations of relative viscosity, at any rate at low Reynolds's numbers (Chap. II, § 6), and the kinetic-energy correction depends on l rather than on l/a. For relative, as distinct from absolute, viscometers it is well to take advantage of the increase in permissible radius which is conditioned by this difference.

If two viscometers of the type here considered are to be designed so as to cover the range from 0·2 cp. to about 500 cp., allowing liquids having viscosities as different as those of ether and of heavy lubricating oils to be tested, the range should be more evenly divided than it is by the two instruments suggested in the last paragraph. The advantage of calibration by means of water is already lost in the second instrument, hence the minimum viscosity which it is designed to measure may be raised to 10 cp. Except in so far as overlapping is desirable, the increase in the product of pressure and of time of flow from the minimum to the maximum of each viscometer is then only 50-fold and a wide range of pressures becomes available in the examination of the more viscous liquids; the occurrence of drainage errors may then be observed or avoided without the need for excessively tedious observations. The calibration of the second viscometer will require the use either of sucrose solutions (relying on the data of Bingham and Jackson, see p. 308) or of a convenient liquid of which the viscosity has been determined in the instrument of lower range.

Bingham's specifications are based on the use of a constant volume of flow of 4 ml.; the minimum time of flow being constant at 200 secs., variations in the diameter of capillary available are off-set by adjustment of the length so that a^4/l remains the same. When the length of the capillary is as much as 20 cm., the complete viscometer will become somewhat inconvenient and fragile; by

way of fixing the overall length approximately, so that thermostatic requirements are not too variable, an alternative method of specification may be suggested, which has been found useful in the design of the British Standard instruments mentioned in § D. According to this method the length of capillary is fixed and approximate constancy of the minimum time of flow is secured by varying the volume of flow to suit the bore; limits are set to the variation permissible by the necessity of avoiding the use of volumes which are either unduly small, entailing errors of measurement, or unduly large, involving waste of liquid and delay in attaining equilibrium of temperature. Let us find, on these lines, the dimensions appropriate to the viscometers, which we shall call A and B, assuming with Bingham that the minimum pressure to be employed is 50 cm. of water, that the maximum allowable for the kinetic-energy term is 5 per cent. and that the minimum time of flow is 200 secs.

In the expression (III. 2)

$$a^4 < \frac{64\eta^2 l^2 \epsilon}{m\rho P}$$

we may put $\epsilon = 0.05$ and $m\rho P = 50,000$ in C.G.S. units approximately. For viscometer A ($\eta > 0.2$ cp.), if l is fixed at the convenient length 10 cm., we thus find that the maximum radius permissible is 0·126 mm. The requisite volume of flow, if the capillary has this radius, is 4·95 ml. Smaller radii and correspondingly smaller volumes are allowable, but it is not advisable to reduce the volume below 2 ml., which would give a time of flow of 200 secs., under the conditions assumed, through a capillary having a radius of 0·101 mm. The tubing selected must thus have a radius between the rather narrow limits 0·101 and 0·126 mm., the volumes varying from 2 to 5 ml.

For viscometer B ($\eta > 10$ cp.), the maximum radius indicated for a length of 10 cm. would be $0.126 \times \sqrt{50}$ mm. and the volume 5×50 ml. Since this volume is obviously unduly large, we may first reduce the length of the capillary to 5 cm. by way of keeping down the overall length of the viscometer; even so, with a permissible radius of 0·63 mm., the volume of flow would still be 125 ml. It will be preferable to use a volume not greater than 30 ml., corresponding with a 5 cm. capillary of radius 0·445 mm.; with these maxima, giving $l/a = 112$, the highest Reynolds's number which will occur in use is 21·5, and the kinetic-energy correction will not exceed 1·2 per cent. The increase in radius

here suggested above that indicated by Bingham is due to neglect of the limitations which he imposes on the ratio of length to radius and on the volume of flow. The greater volume will naturally require a longer time to attain the temperature of a thermostat, but this disadvantage is compensated by the increased ease of cleaning and the reduced liability to obstruction by particles possibly present in viscous media.

3. The Scarpa viscometer. A type of relative viscometer devised by Scarpa[7] has been used by several investigators, particularly in the examination of solutions such as those of soap and glue which are liable to foam and are troublesome to manipulate in the pipettes and pycnometers accessory to the determination of viscosity by Ostwald's method. The form shown in Fig. 18 is due to Farrow:[8] one with a ground-in capillary is described by Masters and Goddard.[9] A volume of liquid, which need not be measured exactly, is introduced into the outer tube and a constant reduced pressure is applied to the top of the 'pipette' while the side arm communicates with the atmosphere. After noting the time t_1 required for the bulb B to be filled, the suction is released and the time t_2 of emptying the bulb is observed. Scarpa at first took the mean of

FIG. 18. Scarpa's viscometer (after Farrow, *Journal of the Chemical Society*).

these two times as proportional to the viscosity, the constant of the apparatus being determined by means of water; later, by eliminating the mean hydrostatic pressure x from the equations

$$\eta = K(P - x\rho g)t_1 = Kx\rho g t_2,$$

where P is the constant suction applied in the first experiment, he arrived at the result

$$\eta = KP\frac{t_1 t_2}{t_1 + t_2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (V.\ 2)$$

where KP is constant for a given arrangement of apparatus.

According to equation (V. 2) the density of the liquid does not enter into the calculation of the viscosity: this is, in fact, one of the

chief advantages claimed for the method. It is obvious that the
kinetic-energy correction has been ignored in this derivation,
although, for the particular case when $t_1 = t_2$, it would reduce η by
twice the usual amount. The correction has been by no means
negligible in the use of some viscometers of this type for which
dimensions have been stated. But even when such a correction
has been introduced or has been made unimportant by the use of
suitable capillaries, the method of calculation remains inadequate
unless a further condition is satisfied, viz. that the change in
hydrostatic pressure during the filling or emptying of the bulb
must not be a large fraction of the mean pressure-difference pro-
ducing the flow. The table (p. 76) indicates, for instance, that if
a cylindrical bulb were used and the initial head were 5/3 of the
final head when t_2 was being determined, the effective mean pres-
sure would be nearly 2 per cent. less than the arithmetic mean
pressure: if the suction applied to the bulb were such as to make
t_1 only half of t_2, the error in the elimination of x to form equation
(V. 2) would amount to about $1\frac{1}{2}$ per cent. and would vary, for a
fixed reading of the manometer, with the density of the liquid
under examination. When an accuracy of 0·1 per cent. is required,
the variation in hydrostatic pressure should not exceed one-tenth
of the mean pressure. Since in some cases it may be inconvenient
to comply with this condition, it should be pointed out that the
error under discussion vanishes when $t_1 = t_2$, i.e., for a symmetrical
bulb, when $P = 2x\rho g$. Since equality of the times also enables them
to be observed with similar accuracy, it should be secured approxi-
mately by adjustment of the arbitrary constant suction when the
calibration is being undertaken. Variation of the ratio $t_1 : t_2$ from
unity in experiments with liquids of different densities will then
incidentally afford some indication of the relation between the
densities. It should be noted that the Scarpa principle does not
allow any considerable reduction of the time of flow of viscous
liquids by variation of the externally applied pressure-difference:
the range of viscosities which may conveniently be measured in any
one instrument is no greater than for Ostwald-type viscometers.

B. Pipette-type Viscometers.

If a capillary be sealed to a bulb provided with two graduations,
observation of the time required for the discharge through the
capillary of the volume of liquid which fills the bulb may obviously

be made to afford an estimate of the kinematic viscosity of the liquid, if the apparatus has been calibrated. 'Pipette' viscometers discharging into the air have been used for many years, their chief virtue being their simplicity, and for rough measurements they have still a certain utility. By placing a water jacket around them it is possible to obtain some degree of temperature control, but part of the capillary is necessarily allowed to protrude below the jacket. The variation of the temperature of the liquid from that of the jacket is minimized, in some designs, by prolonging the jacket below the orifice to form an air pocket similar to that provided in the Redwood No. II or in the Saybolt viscometer. The jet of an ordinary pipette is so short and convergent that the rate of flow through it is proportional to the density rather than to the viscosity, except for very viscous liquids, but by selecting a suitable capillary to replace the jet (or by simply removing the jet, in case very high viscosities are in question) it is possible to obtain approximate comparative tests in the neighbourhood of room temperatures. Pipette viscometers suitable for the examination of glues are discussed by Sheely[10] and a model, which is claimed to give results from which 'Saybolt times' may be obtained with small samples of oil, is described by Ferris.[11]

Apart from any question of kinetic-energy corrections, efflux into air is obviously liable to be affected by the surface tension of the liquid. Some data bearing on this point have already been mentioned (Chap. IV, p. 101), but reference may be made here to experiments by Chéneveau[12] with a jacketed 10 cm.^{3} pipette having a capillary 4 cm. $\times$ 0·15 cm., which gave a time of flow for olive oil of 447 secs. when the discharge was into air, and of 448 secs. when the discharge was submerged. In contrast with this almost inappreciable difference, Ronceray[13] found that at low heads water flowed through a glass capillary 4 per cent. faster when the exit was immersed. Alteration of the angle of contact between the water and the end of the capillary, by coating the glass surface with a thin film of wax, increased the difference between the times for free and submerged discharge. With increasing rates of flow it was observed that when the discharge into air took place from the waxed tip the onset of turbulence was delayed, as indicated either by the appearance of the issuing liquid or by the ratio of the times of discharge. The

capillary used in these experiments had a length of 10·5 cm., a bore of 0·055 cm. and an external diameter of 0·47 cm., and the heads varied from 10 cm. to 170 cm. of water. Some earlier data on the effect of surface tension on the rate of efflux into the air are given by Christiansen.[14]
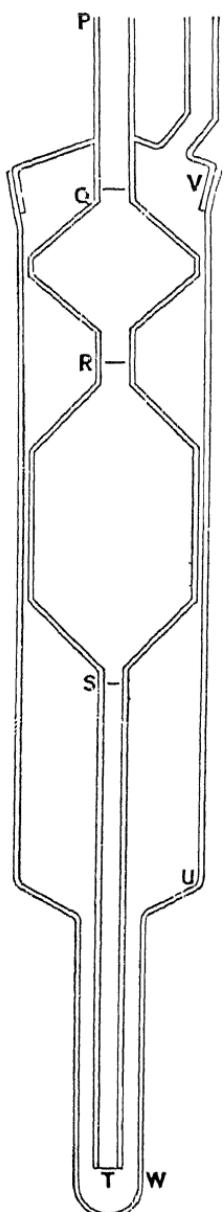
The earliest precise measurements of relative viscosity by a method in which the pressure producing flow was a head of the liquid equal to the length of the capillary appear to be those of Guérout.[15] He used submerged discharge and showed that under these conditions the rate of discharge was independent of the length but varied inversely as the fourth power of the radius of the capillary. A pipette type of viscometer in which the capillary dips below the surface of liquid in a bottle was described in early editions of Kohlrausch's *Lehrbuch der praktischen Physik*:[16] the bottle was provided with a cork through which passed the capillary and an air tube so that the whole could be immersed in water. In such an apparatus the working head is not very accurately reproducible and cannot be made less than the length of the capillary unless a large volume of liquid is used. These defects are avoided in a modification (see Fig. 19) which I described to a sub-committee of the British Engineering Standards Association in 1921.[17] The 'pipette' is enclosed in an outer vessel of slightly greater diameter, which is constricted below the working level; above the bulb which measures the volume of flow there is a second bulb of such capacity that its contents fill the lower part of the outer vessel up to the level *U*. Liquid, at approximately the same temperature as that of the bath, is sucked up from a sample bottle to fill both bulbs of the pipette, to mark *Q*; the pipette is placed in position in the outer vessel

FIG. 19.
Pipette viscometer.

in the thermostat and is allowed to drain. When equilibrium of

temperature has been attained the liquid is sucked up to just above mark R and the fall of the meniscus between marks R and S is timed. Besides reducing the error due to incorrect adjustment of the viscometer to the vertical (§ C 1), this design offers advantages over the usual U-tube forms on the score of easy cleaning. The upper bulb should nearly fill the lumen of the outer vessel, so as to reduce loss of heat by convection from the liquid to the ground-in cap, which may be above the level of the bath. If very precise tests are to be made at temperatures far from that of the room, the diameter of the outer vessel at the working level requires to be considerable (§ C 7): in such an instrument the volume of the upper bulb must be correspondingly large. Dimensions suitable for a set of four viscometers of this type, covering the range from 0·9 to 1,500 cp. and giving times of flow proportional to the kinematic viscosity within at least 0·5 per cent., were published by the British Engineering Standards Association[18] in 1923. Since they have been omitted in the revision of the specification (1929) they are here reproduced for convenience of reference. The principles underlying the design are similar to those explained in § C 6.

Dimensions of Pipette-type Viscometers

Viscometer No.	1	2	3	4
Range (Poises)	0·009–0·072	0·054–0·43	0·32–2·6	1·9–15
Int. Dia. of Tube PQ cm.	0·2	0·5	0·6	0·6
Int. Dia. at R. cm.	0·1	0·4	0·6	0·6
Volume of Bulb RS cc.	1·15	6·5	20	32
Int. Dia. at S cm.	0·10	0·12	0·24	0·4
Capillary ST—Length cm.	10	10	10	10
—Int. Dia. cm.	0·054	0·12	0·24	0·40
Difference between Ext. Dia. of ST and Int. Dia. of UW cm.	0·2	0·2	0·4	0·6
Vertical Distance from Mark S to contraction of Tube at U cm.	4·0	4·0	4·0	4·0

The conical ends of bulb RS have slopes of 45°; the junction at S is trumpet-shaped.

The volume of the bulb QR is such that its contents will fill the outer tube up to U.

Flow times for water, &c., within the limits given in the Table p. 141, for the corresponding U-tube viscometers.

Vogel-Ossag viscometer. A practical form of pipette viscometer with submerged discharge was introduced by Vogel,[19] which presents some features of interest. The 'pipette' (see Fig. 20) is cemented into a metal sleeve which screws into the cap of the reservoir, so that the depth of immersion in the liquid is fixed. The reservoir is double walled, the inner cup being filled to overflowing and the annulus serving to catch the excess. Tests may be made at successively higher temperatures without disturbing the apparatus, the expansion of the liquid causing a little more to overflow at each new temperature. Erk[20] suggested some modification of the thermostat originally supplied, and made the overflow level a little more precise by soldering a small brass hook to the outer wall of the inner cup: this device, indicated in the figure, ensures that the meniscus shall always be of the same shape. Dimensions and tolerances are specified by the Reichsanstalt, which undertakes the determination of the constants of the instruments according to either of two methods of use:

(1) Liquid runs out under its own hydrostatic head, so that times t_k of emptying of the bulb are proportional to kinematic viscosity. The constant applies only when the instrument is used for oils and liquids of similar surface tension.
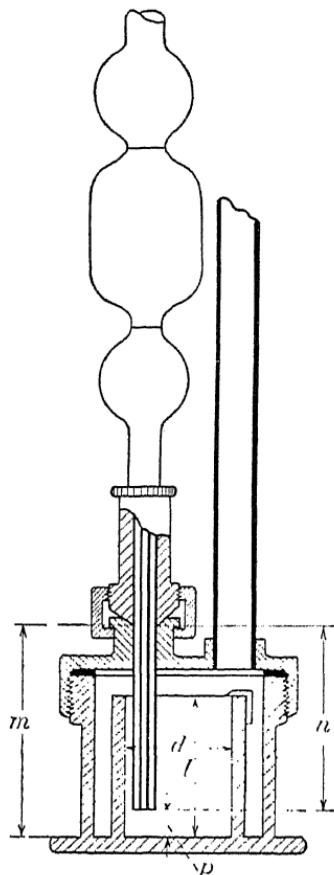
FIG. 20. Vogel-Ossag viscometer (Reichsanstalt specification).

$l = 26 \cdot 0 \pm 0 \cdot 1$ mm.
$m = 41 \cdot 0 \pm 0 \cdot 2$ mm.
$n = 38 \cdot 0 \pm 0 \cdot 2$ mm.
$m - n = p = 3 \cdot 0 \pm 0 \cdot 2$ mm.
$d = 24 \cdot 0 \pm 0 \cdot 2$ mm.

(2) An excess pressure of 60 cm. of water (± 1 per cent.) is applied above the meniscus. The time of flow t_c is then proportional to absolute viscosity, provided the specific gravity of the liquid is between 0·85 and 0·95.

C. Ostwald-type Viscometers.

1. General form. Of the thousands of relative viscosity determinations which have been made during the last forty years in the course of investigations on the liquid state, on solutions and on colloidal systems, it is probable that not less than nine-tenths have been carried out in viscometers of the type first described by
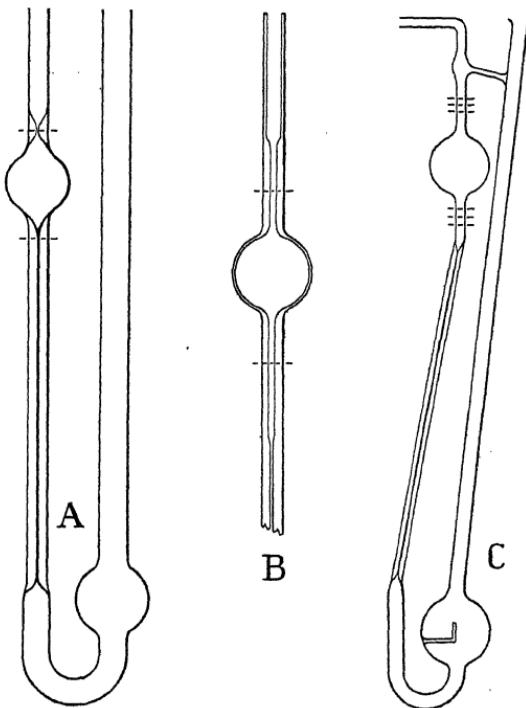
FIG. 21. Ostwald viscometers. A. Original form. B. Measuring bulb according to Jones and Veazey. C. Grüneisen's form.

Ostwald in his *Physico-chemical Measurements*. The Ostwald viscometer is simply a development of the pipette viscometer in which the submerged discharge takes place, not into an external vessel, but into a wide prolongation of the capillary which is bent to form a U-tube. The necessary reproducibility of level in the wide limb is secured by charging the instrument with a constant volume of liquid by means of a pipette of suitable capacity.

In Ostwald's original design (Fig. 21 A) the lower fiducial volume mark is placed on the capillary itself. When the capillary is selected to be of small bore, so that the velocity of flow through

it may be low, the liquid in this arm of the U will come to rest, at the end of a run, at a height above the level in the wider arm which varies with the surface tension. The capillary rise approximates to 10 cm. for water in a tube with a bore of 1/3 mm. Towards the end of an observation, the effective head producing flow may therefore be considerably reduced, by an amount which varies for different liquids. Although the volume contained between the mark on the capillary and the termination of the bulb is normally very small, the error due to this cause may become appreciable owing to the fact that the rate of flow of this volume of liquid is less than the average for the contents of the bulb: if the liquid came to rest at the fiducial mark, the time of flow would obviously become infinite. Quite apart from this theoretical objection, the use of a mark on a fine capillary above or below the bulb entails a practical difficulty in that the drainage of viscous liquids from the walls may be sufficient to produce a bridge across the junction after the rapidly moving meniscus has passed it. It was for this reason that Jones and Veazey[21] adopted the scheme of blowing the bulb in the middle of a piece of wider capillary on which the fiducial marks could be placed (Fig. 21 B). Applebey[22] recognized the possible importance of the surface tension correction: as he had reduced the bore of the capillary to 0·4 mm. and wished to keep the hydrostatic head as low as possible, he placed the lower fiducial mark on the conical junction between the capillary and the measuring bulb; the meniscus then came to rest in the undistorted capillary a few millimetres below the mark. Accuracy in timing is probably secured more easily when the meniscus is travelling with nearly constant velocity, as in the arrangement used by Jones and Veazey, though the length of wide capillary shown above and below the bulb in Fig. 21 B appears unnecessarily great.

If the axes of the limbs of a U-tube are at a distance s apart, the relative error in the mean head h, due to an error θ in the adjustment of the instrument to the vertical, may amount to $1 - \cos\theta \pm \frac{s}{h}\cdot\sin\theta$. For $\theta = 1°$ the cosine error is only 0·02 per cent., but if s is as much as $\frac{1}{2}h$, as appears to be the case in some viscometers which have been described, the last term will become 0·87 per cent. Owing to the fact that error in the final head causes a disproportionately large error in the mean head, the above estimate

should strictly be increased. In order to avoid the sine error, de Jong[23] recommends that instead of adjusting the U-tube so that the limbs are vertical, the viscometer should be tilted and clamped so that the upper bulb is vertically above the lower. The same result is achieved in the form used by Grüneisen[24] in which the capillary is inclined to the axis of the upper bulb as in Fig. 21 c.

2. Special forms. Numerous slightly modified Ostwald viscometers have been described as suitable for particular purposes or as embodying some feature tending towards greater accuracy or convenience. Many of the modifications consist in the sealing of various systems of stop-cocks to the limbs in order that volatile or hygroscopic liquids may be more efficiently conserved, especially during their transference from one bulb to the other (see § C 8). A few forms which present points of interest are here illustrated.

(a) *For use with opaque liquids* which wet glass, the viscometer shown in Fig. 22 is suggested by the British Engineering Standards Association.[25] In an Ostwald viscometer of the usual form the presence of an appreciable thickness of a dark-coloured viscous liquid on the walls interferes with the observation of the fall of the meniscus in the upper bulb. This difficulty is avoided and the error due to variation in the volume of liquid retained on the walls is minimized by observing the *rise* of the meniscus in the initially clean bulb *CD*. The working volume is that required to fill the U-tube from mark *B* to mark *A*: during the introduction and adjustment

Bend Unconstricted
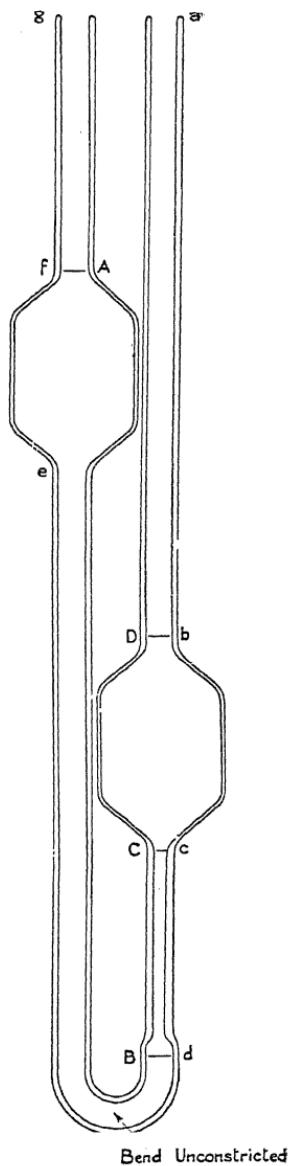
Fig. 22. British Standard viscometer for opaque liquids.

of this volume of liquid, the right limb is closed and the liquid is not allowed to rise above B. On opening a stop-cock above D the capillary and the bulb CD are filled. With care and some patience it is usually possible to make a redetermination of the time of flow after allowing the left-hand limb to drain thoroughly. Dimensions suitable for two instruments having ranges 30–250 cp. and 100–1,500 cp. are tabulated in the specification.

Mention may be here made of a viscometer of somewhat unusual design devised by Lidstone[26] which is also available for use with opaque liquids. It is not in the form of a U-tube, but can hardly be classed with the pipette viscometers. It consists of a vertical capillary connecting a wide tube above it with a graduated bulb below it: a stop-cock is attached a short distance below the bulb. The apparatus is filled with mercury up to the top of the capillary and a roughly measured quantity of the liquid under test is poured into the wide tube so as to form a shallow layer above the mercury. On opening the stop-cock, mercury runs out and draws the liquid through the capillary into the bulb. The time t required for the replacement of the mercury in the bulb by the liquid is observed. When certain rules are observed in the construction, the viscosity may be calculated by the formula

$$\eta = kt(\rho + 13 \cdot 59 f), \quad . \quad . \quad . \quad . \quad . \quad (\text{V. } 3)$$

where k is a constant, determined by means of a liquid of known viscosity, and f is the ratio of the mean length of the mercury column to that of the liquid column during the flow. The theory of the instrument was developed in a note by Barr[27] which indicated also a method of checking whether certain simplifying assumptions are justified by the relation between the dimensions of different parts. Dimensions for a viscometer suitable for the testing of oils were given in the first issue of the British Engineering Standards Association's pamphlet.[28] Owing to the use of mercury, the maximum permissible bore of the capillary is much less than in the U-tube form described above. The instrument needs to be cleaned and refilled before a redetermination of the time of flow can be made.

(b) *For use with liquids which have a high vapour pressure* or are capable of reacting with the oxygen of the air, the form shown in Fig. 23 I has advantages. A known volume of liquid is introduced

at A and the viscometer is sealed near this point (or closed by a tap previously attached): if necessary, the apparatus may be evacuated or filled with inert gas before the liquid is put into it. To make an observation, the instrument is inverted so that the contents of the lower bulb C run through B and fill the upper bulbs D and E. Occasionally a little manipulation may be needed
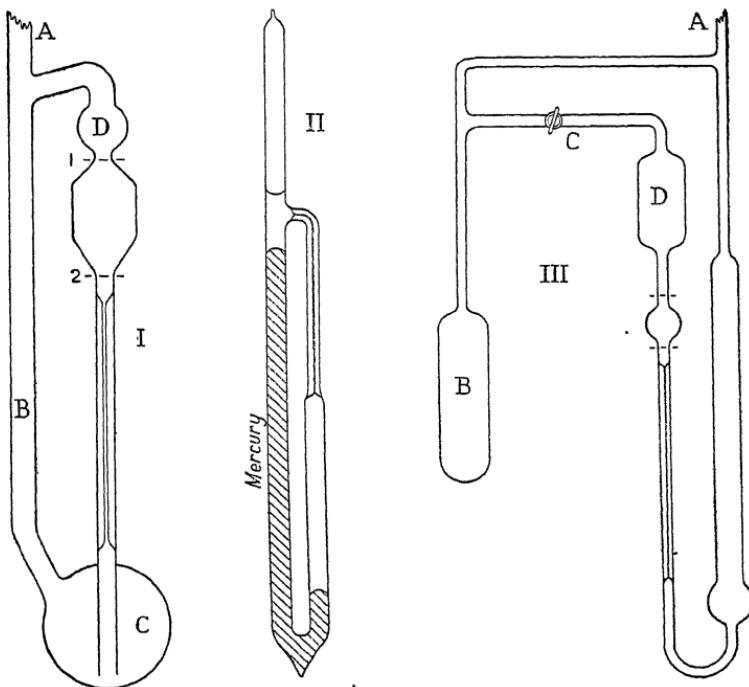
FIG. 23. Viscometers for volatile liquids. I. Kuenen and Visser (modified). II. Heydwiller. III. Maass and Boomer (after the figure in *Journal of the American Chemical Society*).

in order to obtain a continuous thread of liquid in the capillary. On returning the viscometer to the normal position the excess of liquid runs back through B while the contents of D are passing through the capillary: the meniscus is then timed from mark 1 to mark 2 and determinations may be repeated as often as desired, without opening the apparatus. As originally described by Kuenen and Visser[29] (cf. also Lewis[30]) for use with liquid butane, the viscometer was filled through a T-piece sealed half-way up tube B, and the bulb D was absent: the addition of this bulb gives more time for the operator to make adjustments and for the excess of a

viscous liquid in B to return to C. Bulb D probably also reduces the drainage error in the delivery from bulb E; the form shown has been found at the National Physical Laboratory to be suitable for use with liquids having viscosities of a few poises. In Kuenen and Visser's experiments the butane was distilled directly into the apparatus and its volume was not fixed but had to be deduced from the weight: hence, in the calibration by means of water, a series of observations was made with different volumes of water so that the factor corresponding with any given working volume could be found by interpolation.

A viscometer which may be hermetically sealed after the liquid has been distilled into it, *in vacuo* if desired, was described by Heydwiller.[31] The lower half of the wide U-tube (Fig. 23 II) contains mercury; the liquid under examination is added until its level stands a little way above the point at which the capillary is sealed into the left-hand limb. The apparatus is tilted so that the mercury menisci are displaced to the positions indicated, and is then adjusted to the vertical: observation is made of the rate of fall of the mercury column, which is a measure of the rate of flow of the liquid through the capillary. Calculation of viscosity from such observations and a knowledge of the dimensions of the apparatus is somewhat complicated if the kinetic energy correction is not negligible (cf. Chap. III, § 2 B (3) b). If, however, the capillary is of suitable length and bore and a constant volume of mercury is used, viscosities relative to that of a calibrating liquid may be obtained by using the simple formula

$$\eta = k\,(\rho_0 - \rho)\,t, \qquad \ldots \quad \ldots \quad \text{(V. 4)}$$

where ρ_0 is the density of mercury and ρ that of the liquid, and t is the time required for the mercury meniscus to fall from one fixed mark to another: k is a constant obtained in a similar experiment with the standard liquid. It is obvious that the quantity of liquid needs only to exceed a certain minimum: mercury should not be allowed to enter the capillary or to flow so rapidly as to entrap appreciable amounts of liquid on the walls.

A form of Ostwald viscometer in which the liquid levels may be manipulated without making external connexions and without tilting is due to Maass and Boomer.[32] The instrument, shown in Fig. 23 III, is filled with inert gas and a weighed (or measured) quantity of liquid is introduced through a tap at A. Tap C is

closed and bulb B, which is outside the thermostat, is warmed to raise the liquid into the measuring bulb, compressing the gas in the bulb D. The flow is started by opening tap C to equalize the pressures of gas in the two limbs of the viscometer. Maass and Boomer used this viscometer for the examination of liquid ethylene oxide (b.p. $10 \cdot 7^\circ$ C.) and calibrated it by introducing a weight of water having a volume exactly equal to that calculated from the weight and density of the ethylene oxide distilled into it; a curve relating the constant to the working volume would be desirable, as in Kuenen and Visser's method, if any very extended series of observations was to be made.

3. Kinetic-energy correction. In the original description of his viscometer Ostwald recognized that if the rate of flow is high it is necessary to apply a kinetic-energy correction. Without indicating any dimensions other than a length of 10 to 12 cm. for the capillary and a volume for the upper bulb such that the time of flow for water should be not less than 100 secs., he enunciated the formula

$$\frac{\eta}{\eta_s} = \frac{\rho t}{\rho_s t_s}, \quad . \quad . \quad . \quad . \quad \text{(V. 5)}$$

in which η, η_s are the viscosities and ρ, ρ_s the densities of two liquids giving times of flow t, t_s, when equal volumes of them are introduced into the viscometer. If the viscosity of the calibrating liquid be known it becomes possible to calculate a constant K ($= \eta_s/\rho_s t_s$) for the instrument and to write the equation in the convenient form

$$\eta = K\rho t. \quad . \quad . \quad . \quad . \quad \text{(V. 5 a)}$$

In these simple formulae it is tacitly assumed that the kinetic-energy correction is negligible. Unfortunately they have been considered to apply to many instruments without any recognition of the possibility of introducing error by this assumption.

Grüneisen[33] indicated an experimental method for the examination of a viscometer to find over what range of times of flow equation (V. 5) might be regarded as valid. If Poiseuille's Law be applied to a given viscometer, in which the radius and length of the capillary and the volume of flow are fixed, equation (II. 3) reduces to

$$\eta = Pt \times \text{(constant)}.$$

Hence, if observations are made of the time of flow of a certain liquid at a fixed temperature when P is varied, the product Pt will appear to be constant so long as the law is obeyed; only when the rate of flow becomes so great that the kinetic-energy correction is no longer negligible will Pt begin to increase. Grüneisen first determined the effective mean hydrostatic head h_0 in the viscometer by the method described in Chap. III, § 2 B (3) b : this head is that operating during the normal use of the instrument. He then applied various constant measured excesses p_1, p_2, &c. of air pressure above the liquid in the upper bulb and observed the times of flow, t_0, t_1, t_2 &c. The total effective pressure P was then taken to be the sum $h_0 \rho g + p_1$, &c. and the product Pt was plotted against t: Poiseuille's simple law was considered to be valid over the range in which the points lay on a horizontal straight line, a correction term being necessary when the time of flow was further reduced. The method has been used by Applebey,[34] by Merton,[35] and by Washburn and Williams.[36] It is, however, somewhat troublesome, and the experimental determinations of h_0 and of the values of Pt are considerably less accurate than the observations of time of flow and of density on which the normal use of the viscometer depends. Actually, as may be seen from consideration of Koch's logarithmic formula for mean head (III. 9), the range of applicability of Poiseuille's Law is underestimated, since the effective pressure increases more rapidly than do the sums $h_0 \rho g + p_1$, &c.

A simpler and more satisfactory method for the examination of relative viscometers in this connexion is afforded by observation of the times of flow of several liquids of which the kinematic viscosities are known. If the absolute values of viscosities are not available or are of inadequate accuracy, it is sufficient for the purpose in hand to make use of relative values obtained by the use of another Ostwald viscometer in which, for a given liquid, the quotient of the rate of discharge by the length of the capillary is considerably less than in the viscometer under test. For the range of viscosities over which the relative values can be satisfactorily reproduced, the simple equation of Ostwald may be regarded as valid. If a small apparent increase of viscosity is found for the more fluid calibrating liquid, it may be convenient to calculate a constant for a correction term by the following method:

For a viscometer in which V, l, a, and h are fixed, the modified Poiseuille equation (II. 7 a) reduces to

$$\eta = \rho\,(At - B/t), \quad . \quad . \quad . \quad . \quad \text{(V. 6)}$$

where A and B are constants. If ν_1 and ν_2 are the kinematic viscosities of two liquids giving times of flow t_1 and t_2, the two constants may be evaluated as

$$A = \frac{\nu_2 t_2 - \nu_1 t_1}{t_2^2 - t_1^2}, \qquad B = \frac{t_1 t_2}{t_2^2 - t_1^2}\,(\nu_2 t_1 - \nu_1 t_2). \quad . \quad \text{(V. 6 a)}$$

4. The effect of curvature of the capillary. It has not infrequently been suggested that the capillary of a viscometer for relative measurements should be bent into the form of a U, with the object of allowing a greater length to be included without making the instrument any less compact. Pribram and Handl's improved apparatus (§ A 1) had a capillary so bent. Grüneisen[37] investigated the effect of winding the tube into a helix, so that about 1 metre of it could be included in a viscometer small enough to be immersed in a thermostat of the usual moderate dimensions. He found, however, that times of flow in such an instrument were not proportional to kinematic viscosities over any wide range: using a helix of 2 cm. diameter, for example, he observed times of flow for two aqueous solutions of which the ratio differed by 12·4 per cent. from that (1 : 2·74) required by the relative viscosities. He concluded that the radial accelerations in the helix interfered with the normal parabolic distribution of velocities and so produced an increase in the resistance offered by the tube which was a function both of $vd\rho/\eta$ and of v^2/D; (D = diameter of the helix). The occurrence of similar errors in a viscometer with a U-shaped capillary had been previously pointed out by Haffner.[38] The problem of stream-line flow in a curved pipe has recently been studied both theoretically and experimentally by Dean[39] and by White.[40] In practice it is safest to use a straight capillary and to make such bends as are required only in parts where the diameter is several times as great as that of the capillary.

5. Surface tension and drainage errors in Ostwald-type viscometers. Mention has already been made (§ 3) of Grüneisen's method of calculating the mean hydrostatic head in an Ostwald

viscometer. In using this method with water Applebey deduced a mean hydrostatic head of 10·60 cm. for a viscometer which had an upper bulb of some 7 cm.³ capacity and a lower bulb of 3·8 cm. diameter, and observed that this head was 0·39 cm. less than the actual difference of level at mean time. He therefore corrected the times of flow by multiplying them by the factor $\dfrac{10 \cdot 99 - 0 \cdot 39 \gamma / \rho}{10 \cdot 60}$

where γ is the surface tension relative to that of water and ρ is the density of the liquid. In view of the difficulty of determining the mean head, this differential method of obtaining the correction is less accurate than the more direct one, analogous to that of Bénard (Chap. III, § 2 B (3) a), which is applicable when the reservoir into which discharge occurs is of large or uniform diameter. The simplest method of estimating the surface tension error for a completed viscometer appears to be that used by Kuenen and Visser;[41] this is substantially the same as that of Bénard except that the values of the capillary rise at successive positions of the falling meniscus are calculated from measurements of the diameters at those positions, instead of being experimentally determined. The calculated rises are plotted against the times required to reach the different levels; these times are observed directly. The average capillary elevation is found from a planimetric integration of the curve. For a viscometer in which the upper bulb was approximately a sphere of volume 3·5 cm.³, Kuenen and Visser estimated that the mean head of 11·6 cm. was reduced, owing to surface tension, by 0·034 cm., i.e. by 0·3 per cent., when water flowed through it. In obtaining this estimate they calculated capillary rises from the known surface tension γ and the measured radii r by means of the simple formula $h = 2\gamma/(\rho\, gr)$. This formula, however, is quite inadequate; even the more extended equation given by Rayleigh[42] does not hold for diameters of more than a few millimetres. Sugden[43] has indicated how the capillary rise may be calculated for any diameter by making use of the tables prepared by Bashforth and Adams in 1883. According to this method, the rise calculated by means of the simple formula used by Kuenen and Visser must be multiplied by a factor f which depends on the form of the meniscus, i.e. on the value of the ratio r/a where $a = (2\gamma/\rho\, g)^{1/2}$. The value of a being known at the temperature of calibration, and r having been measured at different levels, the factor appropriate to each level

may be deduced by interpolation from the subjoined excerpt from Sugden's table:

Values of f in equation $h = f \cdot a^2/r$

r/a	f	r/a	f	r/a	f	r/a	f
0·00	1·0000	0·70	0·8606	1·40	0·5929	2·10	0·3546
0·10	0·9968	0·80	0·8249	1·50	0·5545	2·20	0·3267
0·20	0·9869	0·90	0·7875	1·60	0·5179	3·0	0·149
0·30	0·9710	1·00	0·7490	1·70	0·4822	4·0	0·056
0·40	0·9498	1·10	0·7098	1·80	0·4480	5·0	0·020
0·50	0·9236	1·20	0·6704	1·90	0·4152	6·0	0·006
0·60	0·8936	1·30	0·6315	2·00	0·3843	—	—

More accurate values of the capillary rise for $r > 2 \cdot 2\,a$ have been calculated by Bosanquet,[44] but the rises are so small in very wide tubes that the approximate factors above included will normally be adequate for the present purpose.

It is obvious, from the rapid variation of f with r/a in the later parts of the table, that capillary rises are not proportional to surface tension. In cases where the correction is important, its value should therefore be calculated by the same method for a second liquid of much lower surface tension than water, so that an estimate may be obtained of the rate of variation of the correction with variation in surface tension.

. General data on the subject of drainage errors, i.e. errors due to the retention of liquid on the walls of a bulb from which the discharge is measured, have already been discussed in Chap. III, § 2 C (3). For any of the relative viscometers described in this chapter the necessary correction will be less than for an absolute instrument having a similar bulb, since it will depend on the *difference* between the errors occurring with the liquid under test and the calibrating liquid respectively. It would appear from equation (III. 13) that in a viscometer of the Ostwald type, in which the rate of fall of the meniscus is inversely proportional to the viscosity, the thickness of the film left on the walls should be approximately constant for different liquids. Moreover, liquids of very widely differing viscosity are not usually compared directly in the same Ostwald instrument; the more viscous liquids may be examined in models possessing large bulbs, in which the drainage error tends to be relatively less owing to the smaller surface per unit volume. When externally applied pressures are to be used to reduce the time of

flow of liquids of high viscosity, as in experiments on the effect of rate of shear, the error should be estimated by preliminary measurements as in absolute viscometry (Chap. III, § 2 C (3)).

It should be remarked that the possibility of occurrence of drainage errors is not absent even in viscometers, such as that of Bousfield (Fig. 26) and the 'opaque liquid' apparatus of the British Engineering Standards Association (Fig. 22), in which the time of filling of a bulb is measured: for the thickness of the film of liquid left in the higher bulb influences the value of the mean head.

6. Dimensions. It is desirable that Ostwald viscometers for general routine work should be so designed that times of flow shall be proportional to kinematic viscosities, within the desired limit of accuracy, down to the lowest viscosity for which the instrument is suitable. As already mentioned, this proportionality has been very commonly assumed for all viscometers giving times of flow greater than some 100 secs.; if a second constant is necessary it is liable to be forgotten after numerous tests have been made with liquids so viscous that the kinetic-energy term has been negligible. By so designing the apparatus that the term may always be neglected, above a certain viscosity which is sufficiently well indicated by the time of flow, the calibration is simplified, especially in the higher ranges where liquids of known viscosity are not easily available. Only for routine work on liquids having viscosities less than that of water (e.g. petrols) should I recommend a two-constant viscometer: here the bore which is necessary in order to render the correction term negligible becomes so restricted as to be troublesome in use, and a flow time of 100 secs. then requires a bulb so small that surface-tension errors are likely to become appreciable. The diameter of the capillary may be almost doubled and the volume increased tenfold if the kinetic-energy term be allowed to reach 1 per cent. instead of being less than 0·1 per cent.

Grüneisen[45] appears to have been the first to make any serious effort to find data for the design of a viscometer in which the departures from proportionality between viscosity and time of flow should cause less than a certain stated error. From an analysis of Poiseuille's data he concluded that the usual kinetic-energy correction should not be applied to viscometers with submerged discharge but that the error was a function of vd and of l/d ($v =$ linear velocity of flow of water, $d =$ diameter and

$l =$ length of capillary). He proceeded to plot three curves showing the values of vd for which the relative errors ϵ amounted to 0·1, 1·0, and 5 per cent. respectively when different ratios of length to diameter were employed. Flowers[46] made these curves more generally applicable by replotting them with log $(vd\rho/\eta)$ as ordinate and $\log l/d$ as abscissa. In this form the data used by Grüneisen become available for the estimation of the error occurring in any given viscometer when a liquid of stated kinematic viscosity is used therein. For purposes of design it is necessary, in order to find the required diameter of capillary, to assume certain lengths and mean heads and then to make a series of approximations. To render the data more readily applicable, I made[47] the tentative assumptions $l = 10$ cm. and $h = 5$ cm. $= \frac{1}{2} l$ and replotted Flowers's curves on a diagram (Fig. 24 full curves) with ordinates log 1000 η/ρ and abcissae log 100 d. The curves thus indicate directly the maximum diameter of capillary which may be employed in a viscometer destined for use with liquids of which the viscosity may fall to a stated minimum when it is required that the error shall not exceed 0·1 per cent., 0·5 per cent., or 1·0 per cent. As an alternative to the use of Grüneisen's criteria, the dotted curves show the diameters calculated, for the same assumed length and head, by postulating that the usual kinetic-energy term shall not exceed the stated percentages of the viscosity, i.e. that

$$\frac{m\rho vd}{32\,\eta} < \epsilon\frac{l}{d} \qquad [m \text{ is taken as unity}] \quad . \quad . \quad \text{(V. 7)}$$

A modification of this second criterion has been put forward by Dorsey;[48] after a pungent criticism of Grüneisen's method of dealing with the problem he shows that more recent experiments by Bond lead to the requirement

$$\frac{m\rho vd}{32\,\eta} < \epsilon\left\{\frac{l}{d} + 0\cdot573\left(1 + \frac{1}{2\,\epsilon}\right)\right\}. \quad . \quad . \quad \text{(V. 7 a)}$$

(The coefficient 0·573 and the value of m may vary with the end conditions, and below $vd\rho/\eta = 10$ the error ϵ becomes zero.) The interpretation of Bond's data has been discussed in an earlier section (Chap. II, § 6 (e)), but it will be seen that Dorsey's criterion permits the use of a larger diameter than does (V. 7). Hence in designing an instrument to deal with liquids having viscosities not less than a stated minimum, all the criteria proposed will be

satisfied if a capillary be selected of which the diameter does not exceed the smaller value of the two indicated by the curves of Fig. 24 for a given relative error.

If the mean head is equal to, instead of being half of the length of the capillary, this being still 10 cm., Fig. 24 may be used by shifting the curves upwards and parallel to themselves a distance 0·15 scale units along the axis of log ν. If both the length of the capillary and the mean head are supposed to be equal to 5 cm., the dashed curves will require to be raised by 0·30 scale units and the full curves by approximately the same amount.

The mean head, which is assumed in deriving an estimate of the maximum diameter of capillary from Fig. 24 or from the more general equations on which the curves are based, should not be reduced unduly. The maximum diameter permissible for a given kinetic-energy error does not increase at all rapidly with decrease of head; on the other hand errors, due (1) to inaccuracy of levelling (cf. p. 120), (2) to variations in the working volume of liquid introduced into the viscometer (cf. p. 134) and (3) to differences in surface tension between the liquids which are to be compared, tend to become important when the final head is made less than a few centimetres. The maximum diameter for the capillary increases only with the fourth root of the length of the capillary, for a kinetic-energy correction of a given relative amount. There is therefore no advantage, from this point of view, in selecting a length which may involve increased fragility and make the necessary thermostat inconveniently deep). A length of some 10 cm. appears to be fairly generally suitable.

Let us suppose that a length of 10 cm. has been selected for the capillary, that a mean head of 5 or 10 cm. has been assumed and that the maximum diameter which may be used for the capillary has been obtained from Fig. 24 after postulating the accuracy which is required and the minimum viscosity which the instrument is to measure. The accuracy obtainable in the measurement of the time of flow (say 0·2 sec. for a stop-watch) imposes a lower limit on the time and hence on the volume of flow. In order that experiments with the more viscous liquids may not be unduly prolonged it is advisable that the volume of the upper bulb should approximate to that which may be calculated on the stated assumptions. It will be found, however, that the volume so estimated becomes less than 1 ml. when an accuracy of 0·1 per cent. is desired in the

determination of viscosities less than that of water: in this case
one is therefore obliged to increase the volume and to tolerate the
inconvenience of a minimum time of flow considerably greater than
200 secs. in order that errors due to surface tension may not be
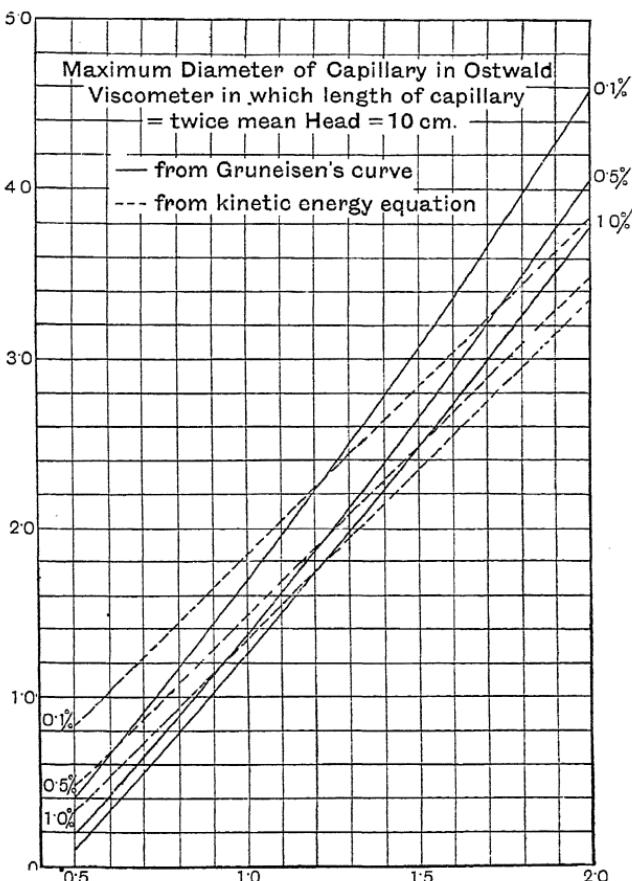
FIG. 24. Chart for estimating maximum permissible diameter
of capillary (after the figure in the *Journal of Scientific
Instruments*): ordinates log 1000 η/ρ, abscissae log 100 d.

introduced by the use of a bulb of small diameter. When the mini-
mum viscosity to be measured is of the order of one poise and an
accuracy of 1 per cent. is sufficient, the volume calculated by the
method indicated becomes greater than 50 ml.: since an Ostwald
instrument with such a volume would be inconveniently.large, the
volume may be reduced by the simple expedient of employing a
capillary of smaller bore than the maximum allowable. In this
range the diameter of the capillary suggested by Fig. 24 is so

considerable that moderate reduction of it will not entail much increase in the liability to obstruction or in the difficulty of cleaning. It may be remarked that very large bulbs are objectionable, not only because of the waste of liquid and of the length of time required for thermal equilibrium, but because the reduction of the final head and the increased separation between the limbs of the U-tube necessitate greater precision in the adjustment of the viscometer to the vertical.

The double-cone shape suggested by Bingham for the bulb of his pressure-type viscometers would lead to inconveniently large diameters for bulbs having capacities up to 30 ml. The advantage of good drainage may be retained however by inserting a cylindrical portion between the two right 45° cones: for minimum surface area the cylindrical portion of a bulb of this form requires to have a length of 0·8 times the radius, but for the largest bulbs this length may well be increased to about $1\frac{1}{2}$ radii.

Dimensions suitable for two Ostwald viscometers, designed in accordance with the above principles to give an accuracy of better than 0·5 per cent. in the ranges 0·9 to 43 cp., are detailed in an appendix to the recently revised specification of the British Engineering Standards Association.[49] Both are filled by means of 20 ml. pipettes.

7. Working volume. Ostwald viscometers require to be filled with a constant working volume of liquid. The error in time of flow produced by a given error in working volume may be calculated from the dimensions of the apparatus: it is obviously inversely proportional to the mean head and to the mean area of cross-section of that part of the lower reservoir over which the liquid surface rises during an experiment. In a fused-quartz viscometer designed for accurate relative measurements on water, Washburn and Williams[50] made the mean head, and the length of the 0·049 mm. diameter capillary, about 20 cm. Although the volume of flow was only 9 cm.³, the lower bulb had a much greater capacity and was of an oblate spheroidal shape (maximum diameter 8 cm.). Assuming that the working volume, of 65 cm.³, was such as to bring the level of liquid in the large bulb to the maximum diameter, an excess of 2 cm.³ in the delivery of the pipette used for filling would have raised this level by 0·04 cm.: the consequent reduction in mean head and increase in time of flow would thus

have amounted to 0·2 per cent. Washburn and Williams record an observation of time of flow made with an excess filling of 2 cm.³, which was only 0·08 per cent. less than that obtained with normal filling: their small corrections for thermal expansion, which are based on this experiment, appear to require examination, though their statement that errors of delivery of the pipette are likely to produce only negligible errors in most relative viscosity determinations with such an instrument may well be accepted.

The volume of liquid required in the Washburn and Williams viscometer may be inconvenient in some cases, and the distance between the axes of the limbs of the U-tube necessitates considerable care in the adjustment of the instrument to the vertical. With liquids more viscous than were used by them, errors in delivery of the pipette may become important even with so wide a recipient as theirs. This type of error is avoided in the procedure adopted by Grüneisen and by Erk,[51] who introduced into their viscometers weights of liquid equal to a constant multiplied by the (apparent) density of the liquid. Such a method of filling is inconvenient for routine work; when determinations have to be made at several temperatures the adjustment of weight has to be repeated for each temperature unless corrections can be made with sufficient accuracy.

When a fixed working volume is measured into the viscometer at a certain temperature, either by weighing or by delivery from a graduated pipette, and the viscosity is required at a different temperature, the expansion or contraction of the liquid necessitates the application of a correction which may be estimated in either of two ways:

(a) Let the density of the liquid at the temperature θ_0 at which the working volume V is measured be ρ_0 and let that at the temperature θ_1 of experiment be ρ_1: if the adjustment is by weighing, the weight introduced is $V\rho_0$. Then the volume at the temperature θ_1 will be $V\rho_0/\rho_1$, and the change in working volume will be $V(\rho_0/\rho_1 - 1)$. Two experiments are made with a given liquid at θ_0, first with the normal working volume and then with an additional volume δV, of the same order as the expansion just calculated: let the observed times of flow be t and $t + \delta t$. The mean hydrostatic heads in these two experiments with volumes V and $V + \delta V$ must have been in the ratio of $t + \delta t$ to t; hence an increase of $V(\rho_0/\rho_1 - 1)$

in the working volume would reduce the mean head by

$$\frac{V(\rho_0/\rho_1-1)}{\delta V}\cdot\frac{\delta t}{t+\delta t}$$

of its value. The viscosity η_1 of the liquid at the temperature θ_1 at which it gives a time of flow t_1 is therefore equal, not to $K\rho_1 t_1$ (cf. equation V. 5 a) but to

$$\eta_1 = K\rho_1 t_1\left\{1-\frac{V(\rho_0-\rho_1)\cdot\delta t}{\rho_1\cdot\delta V(t+\delta t)}\right\}\quad.\quad.\quad.\quad\text{(V. 8)}$$

(b) When the mean head is not too small and the area of cross-section of that part of the lower bulb over which the free surface of the liquid moves during an experiment is large, an approximate value for the correction may be deduced from the dimensions of the viscometer. The mean head h is found by measuring the vertical distance between the bulbs and applying Koch's formula (III. 9). If the area of cross-section of the lower bulb at the level of the liquid is A, the reduction of head due to the expansion of the liquid is $\frac{V}{A}(\rho_0/\rho_1-1)$: the correcting factor to be introduced on the right of equation (V. 5 a) thus becomes

$$\left\{1-\frac{V}{Ah}\left(\frac{\rho_0-\rho_1}{\rho_1}\right)\right\}.\quad.\quad.\quad.\quad.\quad\text{(V. 8 a)}$$

8. Attachments to Ostwald-type viscometers. The liquid might be transferred into the measuring bulb of any of the Ostwald-type viscometers above described by merely attaching a rubber tube to one limb and blowing or sucking through this tube, which would be left open to the air or removed when the observation of time of efflux was being made. In working with non-volatile and non-hygroscopic liquids this simple method of procedure becomes satisfactory if suitable dust-traps are provided to filter the air which enters the viscometer. In the majority of cases it is preferable to connect the two limbs by means of a stop-cock, which is closed during the elevation and is opened during the descent of the liquid: while the flow is being timed, no air need then enter or leave the viscometer and the tubes communicating with the atmosphere may be closed. The simple attachment illustrated in Fig. 25 A is due to Applebey:[52] the bulbs contain tight cotton-wool plugs which are usually moistened with a little solvent if solutions in volatile liquids are under test; the rubber

tubing at the top is pinched while the liquid is being blown into the upper bulb. When the viscometer has a capillary of small bore, rubber tubing may give trouble: the form shown in Fig. 25 B is better, since the bungs (bored eccentrically to allow adjustment) may be placed in position before the apparatus is cleaned: if the stop-cock has a bore greater than that of the capillary and is not obstructed, the resistance to the flow of air through it will be negligibly small.

Washburn and Williams[50] used a special form of three-way cock in an attachment to their viscometer. Several viscometers have been described in which the taps necessary to isolate each limb from the air and to put the two limbs into communication with one
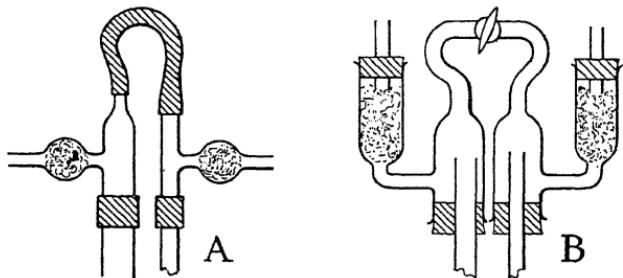

Fig. 25. Attachments to Ostwald viscometers.

another are an integral part of the apparatus. The simplest of these, with the communicating tap only, is due to McIntosh:[53] one which includes also a side tube containing a filter disk has recently been used by Walden, Ulich and Birr.[54]

D. Self-contained U-tube Viscometers.

Errors due to differences in delivery of the pipette used for filling Ostwald viscometers are eliminated and the readjustment of the working volume at different temperatures is facilitated by so designing the viscometer that the volume of liquid introduced may be defined by the construction. A relative viscometer embodying the over-flow device used in Thorpe and Rodger's absolute instrument was described by Bousfield in 1905[55] and again, with certain improvements, in 1915:[56] the essential features are shown in Fig. 26. The capillary A B, some 10 cm. long, had a bore of about 0·1 mm., and the bulb D a capacity of the order of 50 cm.[3] The instrument was filled by dipping the end T of the side tube F into the liquid and applying suction above E, while H was closed, until E contained more than enough to fill D; after closing tap V,

the excess of liquid was allowed to overflow at G, being removed if necessary by sucking it out of the tube sealed into the side of H. Exact adjustment of volume was made, after temperature equilibrium with the bath had been attained, by manipulating tap V till the liquid levels stood at the top of the jet G and at the constriction K: the bores here were about 1 mm. To make an observation,
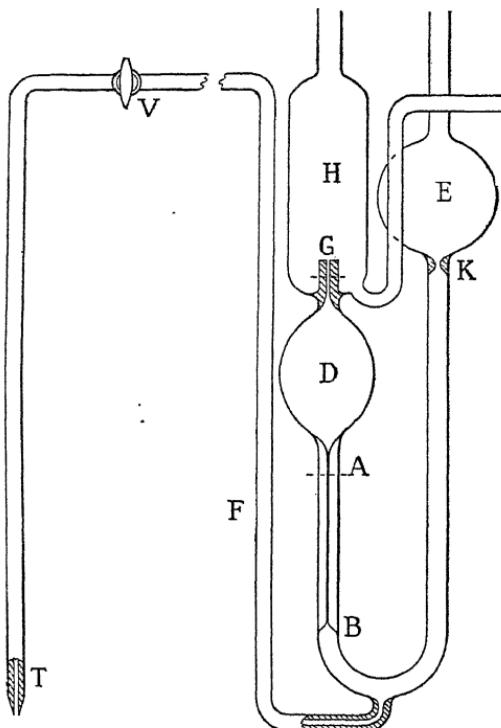
FIG. 26. Bousfield's viscometer (after the figure in the *Journal of the Chemical Society*).

the liquid was sucked up into E until the meniscus on the left fell to a mark about 1 cm. below the junction of D with A B and the time required to fill D to a mark about 5 mm. below the tip of the jet was noted. Readjustment of the volume for different temperatures was easily effected. The constants A and B of equation (V. 6) were found from observations on water at different temperatures: in the 1915 instrument the time of flow for water at $18°$ C. was 472 ± 2 secs., the kinetic-energy term amounting to 3 per cent. at this temperature. The inconstancy of the water rate, upon which Bousfield comments, may have been due to errors in adjustment
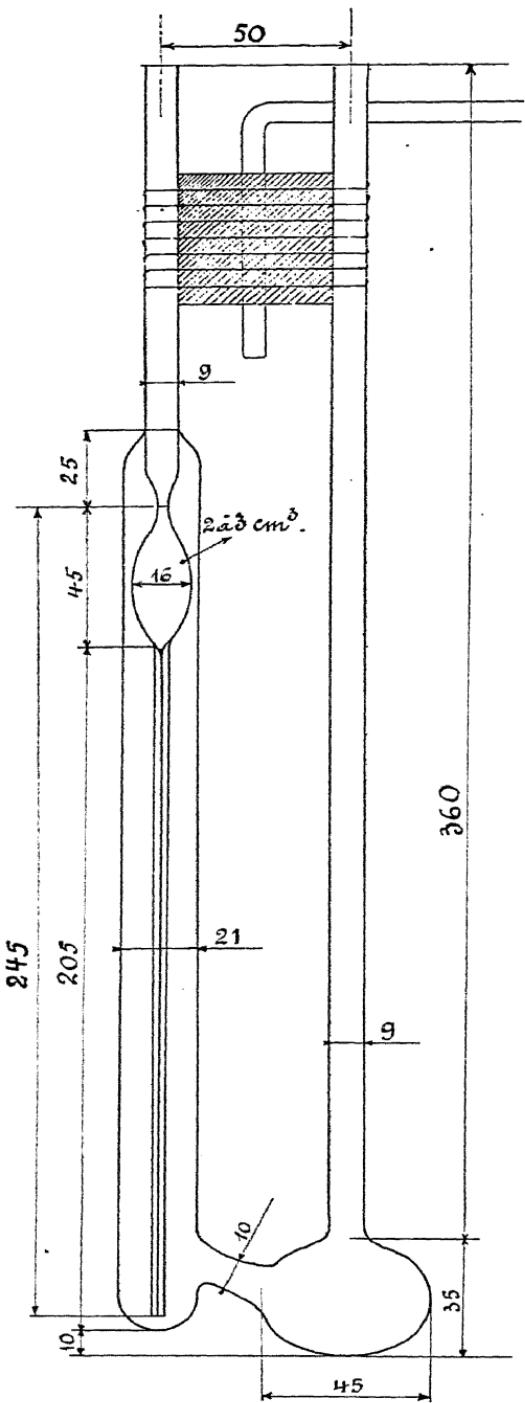
Fig. 27. Martin's viscometer (modified by Timmermans). Dimensions in mm.

of the liquid to the vertical, concerning which he gives no details: with a final head less than 1 cm. and a distance of 6–7 cm. between axes the precision of this adjustment would need to be very high. The final head might be increased by placing the upper timing mark lower down on a longer tube above bulb D, a small bulb being blown between the mark and the overflow jet so that the level of the liquid in E should not be falling rapidly towards the end of an observation: the consequent increase in mean head would naturally necessitate the use of a slightly narrower capillary to give the same time of flow. The siphon filling tube FT does not appear to be essential: its omission would make the instrument much more simple and robust.

Bend Unconstricted

FIG. 28.

British Standard U-tube viscometer.

Automatic adjustment of the working volume is also secured in a viscometer of the pipette type described by Martin.[57] Fig. 27, which illustrates a slightly modified form of Martin's viscometer, has been prepared from a drawing kindly supplied by Professor J. Timmermans; he informs me that experience at the Bureau d'Étalons physico-chimiques (Brussels) has shown this form to retain all the advantages of the original design—in which only the lower end of the capillary was enclosed—and to be less fragile. After the introduction of a suitable excess of liquid into the right-hand side, the instrument is tilted and the left-hand limb is filled, by suction, to a level a little above the top of the elongated measuring bulb; when the vertical position has been restored, a pool of liquid covers the lower end of the capillary. On releasing the suction to make an observation, the liquid issuing from the capillary overflows into the wider reservoir on the right. Re-determinations may be made at higher or at lower temperatures without altering the quantity of liquid in the viscometer. A suitable method of clamping should be adopted such that restoration of the instrument to the vertical does not involve any tedious adjustments. For work with liquids having viscosities as low as that of ether, Martin suggests a diameter of less than 0·3 mm. for the capillary; this may be increased to 0·4 mm.
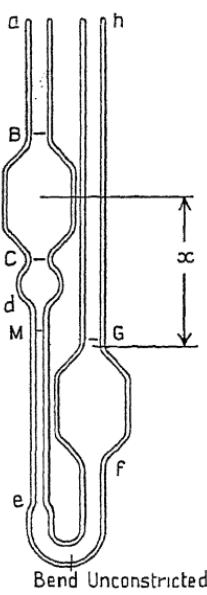
for viscosities over 1 cp. without making the kinetic-energy correction unduly important.

In the U-tube viscometers (Fig. 28) specified by the British Engineering Standards Association[58] two fiducial marks are provided to define the working volume: one mark, G, is etched on the tubing just above the lower bulb and the second, M, is on the capillary at a rather higher level. The quantity of liquid is adjusted by means of a piece of drawn-out tubing so that the menisci in the two limbs coincide with these marks: the adjustment requires to be repeated if the temperature is altered. In order that the final head may not fall so low as to cause an error of 0·5 per cent. when there is a deviation of 1° from the vertical, the small bulb Cd is blown between the capillary and the bulb BC: when, in an experiment, the meniscus in the left limb has fallen to C that in the right limb is thus still in the wide part of the bulb Gf.

Dimensions of British Standard U-tube Viscometers

Viscometer No.	1	2	3	4
Range (centipoises) .	0·9–7·2	5·4–43	32–260	190–1500
Tube aB, length	7	7	7	7
„ diam.	0·3	0·5	0·7	0·7
Bulb BC capacity	1·15	6·5	20	32
„ diam.	1·2	2·0	2·8	3·2
Bulb Cd capacity .	0·1	0·4	1·2	1·4
Capillary de length	10	10	10	10
„ diam. .	0·054	0·120	0·24	0·40
Bent tube ef min. diam. .	0·3	0·5	0·7	0·8
Bulb fG min. capacity	1·25	7·0	21·5	33·5
diam.	1·2	2·0	2·8	3·2
Tube Gh diam.	0·3	0·5	0·7	0·8
Dimension x .	3·9	5·6	5·7	7·1
Distance between axes	1·1	1·6	2·1	2·3
Vertical distance of M above G	0·6	0·3	0·12	0·1
Time of flow at 20° C. for	water	glycerine soln.*	rape oil	castor oil
secs. .	95–150	80–130	300–490	460–730

Capacities are in cm³., linear dimensions in cm. : diameters are internal and the diameter at C is the same as that given for aB.

The bulb fG may be extended towards the bend, making its capacity greater than the minimum given: capacity for Cd may vary by 20 per cent.

* sp. gr. 1·136 at 60° F.

These U-tube viscometers are intended for technical work in which an accuracy of 0·5 per cent. is usually ample. The dimensions have been selected in accordance with the principles set out in § C 6 so that, to this order of accuracy, the kinetic-energy correction may be neglected and one constant only need be determined in the calibration. The volume of bulb BC is such as to give a time of flow of 95 to 150 secs. for the least viscous liquid which is to be used in the instrument: by dividing the range of viscosities between 0·9 cp. and 1500 cp. into four intervals it is thus unnecessary for any test to occupy longer than 15 minutes. In the table on the preceding page, which has been abstracted from the specification, the diameter of the capillary is the maximum which is allowed for each viscometer: diameters one quarter less are permitted, and the volumes &c., corresponding with these and intermediate diameters are tabulated in the pamphlet.

E. Adjustment to the Vertical.

In the use of any of the viscometers described in this chapter it is essential that the hydrostatic head be the same as in the calibration. The position of the instrument relative to the vertical must therefore be reproduced with an accuracy which depends on the construction adopted. In those cases where an external pressure is applied the hydrostatic head will amount normally to not more than some 3 per cent. of the total, so that considerable tolerance is allowable. In the pipette and Ostwald types the time of flow is directly proportional to the hydrostatic head: in the former, and in Grüneisen's and de Jong's modifications, the relative error is therefore $(1 - \cos\theta)$ where θ is the deviation from the vertical: in U-tube viscometers it may amount to $1 - \cos\theta \pm \dfrac{s}{h}\sin\theta$ (see § C. 1).

Since the capillary is nominally straight and usually 5 to 10 cm. long, it is natural to specify the position in which tests are to be made as that in which the capillary is vertical (except, of course, in modifications such as those above mentioned): the tubing above the lower bulb of a U-tube viscometer is however more closely accessible and is generally at least as long as the capillary, so that it may sometimes be more convenient to take its axis as the reference line. Instead of adjusting one of these tubes to the vertical by means of two plumb lines every time the viscometer is placed in the thermostat, it is desirable, if any extended series of observa-

tions is to be made, to provide some rigid stand, fixed to the thermostat or to the bench, or preferably protruding from the wall of the laboratory. The limb which is required to be vertical may be clipped into two V-grooves on a vertical rod, the other limb resting against a flat on a horizontal bar; the vertical rod is fixed to a plate or framework which may either be clamped in a defined position to the rigid stand or else rest on levelling screws by means of which the framework is adjusted to be horizontal. An illustration showing the former arrangement will be found in Applebey's paper:[52] Bingham[59] describes a thermostat with grooves on the sides into which slides the frame carrying the viscometer.

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FLOW BETWEEN PARALLEL PLANES

A. Flow between fixed plates. The equation for the distribution of velocities in the case of a viscous liquid in laminar flow between two infinite parallel planes is derived rather more easily than that for flow in a cylindrical tube. If the planes are at a distance $2h$ apart, the velocity u in a plane at a distance z from the median is given by

$$u = \frac{\Pi}{2\,\eta}\,(h^2 - z^2),$$

and the volume Q discharged per second from a width $2b$ becomes

$$Q = \frac{4\,\Pi}{3\,\eta}\,bh^3, \qquad \ldots \quad \text{(VI. 1)}$$

where $-\Pi$ is the constant pressure gradient measured in the direction of flow (Brillouin,[1] Lamb[2]).

It will be seen that the distance $2h$ between the planes enters into equation (VI. 1) to the third power only and does not therefore need to be measured with quite as high accuracy as the diameter of a capillary tube in order to allow absolute determinations of viscosity to be made. The principle does not appear to have been applied for this purpose, though Davies and White[3] have made a fairly detailed study of the conditions for the transition from laminar to turbulent flow of water between brass plates: they found that turbulence could not persist at velocities lower than those corresponding with $2vh\rho/\eta = 890$ (compare Reynolds's criterion (II. 12) for a circular section). It is usual to compare the flow through pipes of different shape on the basis of the 'hydraulic mean depth' $m = $ (area of cross-section)/(perimeter). Cornish[4] shows that the critical value of vm/ν increases only slightly with increased flattening of the cross-section. Above the critical point the curve relating resistance to vm/ν appears to be the same for all shapes of pipe: for a circular pipe $vm/\nu = \frac{1}{4}\,vd/\nu$.

Long cylindrical capillary tubes cannot be prepared mechanically nor can the variations of diameter at different sections or in different directions in the same cross-section be measured with the highest accuracy. Flat plates, e.g. of steel, glass or fused quartz, can be ground and examined with extreme precision: and a 'capillary cell' of glass with plane parallel walls might be tested,

after assembly, by interferometric methods. For investigatory purposes it should be possible to make the distance between the plates variable at will by building up the cells from slabs of different thickness, e.g. by resting one plate and two side blocks of slightly greater depth on a flat surface and laying the second plate above them. By such variation the effect of the side boundaries could be estimated experimentally.

Equation (VI. 1) applies to flow between planes of infinite width. The rate of discharge will obviously be reduced to some extent by the presence of lateral walls. The formulae for flow through a rectangular pipe appear to have been first worked out by Boussinesq[5] in a paper which is not easily accessible, using a Fourier series. Rowell and Finlayson[6] give a formula which may be re-written for a rectangle of sides $2b$ and $2h$ as

$$Q = \frac{4}{3}\frac{\Pi}{\eta}bh^3\left(1-x\frac{h}{b}\right), \quad . \quad . \quad . \quad (VI.\ 2)$$

where $\qquad x = \frac{192}{\pi^5}\sum_{n=1}^{n=\infty}\left(\frac{1}{n^5}\tanh\frac{n\pi b}{2h}\right)$ with n odd.

They tabulate values of a function simply related to x, from which the following may be derived by a little manipulation:

$b/h =$	1·0000	1·3644	1·4659	1·9520	2·1988	2·8597
$x =$	0·5781	0·6132	0·6176	0·6275	0·6285*	0·6300.

As b/h tends towards infinity, x tends towards the limiting value 0·63025. The derivation of equation (VI. 2) is also given by Cornish,[4] who found agreement between it and his experimental results for a pipe having $b/h = 2·92$. In one series of measurements made by Davies and White[3] where b/h was as low as 40, the correction to the simple equation (VI. 1) would have amounted to 1·6 per cent., according to this calculation.

The disturbing effect of the edges may of course be avoided by substituting for the rectangular cross-section that of a narrow annulus: when the radii of the circles defining the annulus differ by only a small amount formula (IV. 7) may be simplified, as Brillouin showed, to one involving the cube of the difference. As is indicated on p. 104, however, the error due to eccentricity is important: further, the accuracy with which a long outer tube can

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* A slight arithmetical error has here been corrected: the value B = 0·13135 given in the table by R. and F. should be 0·13086.

be bored or drawn is not likely to equal that obtainable with a plane surface.

Gümbel[7] proposed to secure the advantages offered by the use of parallel planes, particularly the possibility of varying their separation to suit different ranges of viscosity, by causing the flow to occur in a radial direction between two parallel annular plates.
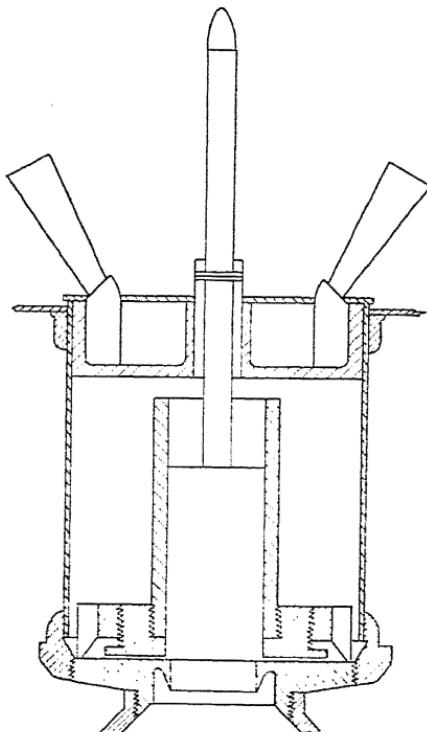
FIG. 29. Gümbel's viscometer (after the figure in *Zeitschrift für technische Physik*).

A diagram of his apparatus is shown in Fig. 29. The inner and outer radii of the annulus through which the liquid was discharged inwards were 15 and 40 mm.; he used a head of 121 mm. and varied the distance between the plates from about 0·2 mm. to 0·4 mm. He was unable, however, to measure the separation with the accuracy needed for absolute determinations and was obliged to estimate the effective aperture from a calibration with water. It is conceivable that improvements in design and construction might remedy this defect.

The formula given by Gümbel for the rate of discharge through

such a viscometer contains some errors which were pointed out by Schiller.[8] The corrected equation is

$$Q = \frac{\pi h^3 H \rho g}{6 \eta \log_e R_2/R_1}, \quad \cdot \quad \cdot \quad \cdot \quad \text{(VI. 3)}$$

where R_2 is the outer and R_1 the inner radius, h is here the distance between the planes, and H is the effective head. The effective head is obtained by subtracting from the total head a kinetic-energy correction of the usual form $m \rho v^2$, in which m has the value 0·771 for discharge from parallel plates and v is equal to $Q/(2 \pi R_1 h)$ when the discharge occurs at the radius R_1.

Equation (VI. 3) is derived on the assumption that the forces opposing the flow in the slit are purely viscous. It is obvious, however, that since the liquid is being accelerated all the way a term involving density should appear in the differential equation. The insertion of this term renders the solution somewhat complicated, but to a first approximation I find that for low Reynolds's numbers and narrow slits the effect is to increase the kinetic-energy correction to $(2 - R_1^2/R_2^2)$ times that indicated by Schiller. With the dimensions used by Gümbel this modification would multiply the correction by 1·86.

B. The rate of approach of parallel plates: Michell's viscometer.

If two plane and parallel plates are separated by a layer of liquid and are caused to approach one another by the application of pressures normal to their surfaces, flow of the liquid must occur from the central to the peripheral regions. If the distance between the plates is small in relation to their area and the rate of approach is slow, it may be shown that the flow is practically laminar. For the time t required for the initial separation H_0 of circular disks of radius a to be reduced to H_1 when a force F is applied so as to cause no disturbance of the parallelism of the surfaces, the calculations of Reynolds[9] give

$$t = \frac{3 \pi \eta a^4}{4 F} \left\{ \frac{1}{H_1^2} - \frac{1}{H_0^2} \right\}. \quad \cdot \quad \cdot \quad \cdot \quad \text{(VI. 4).}$$

This equation indicates the possibility of determining viscosities by means of observations of t and H. Fabry and Perot[10] made such observations in connexion with the adjustment of their absolute electrometer, which consisted of two lightly silvered horizontal glass plates separated by a layer of air: the rate of approach was

deduced from the movement of interference fringes. The fixed disk was 6 cm. in diameter and a somewhat larger disk was supported above and parallel to it by three long flat springs which also acted as guides to maintain the moving disk horizontal. The initial distance between the plates, some 0·1 mm., was measured by superposition of the fringes from sodium and lithium light, a load of 22 mgm. was deposited on the centre of the upper plate and the times of passage of 17 fringes were noted. The increased flexure of the springs caused the disk to tend towards a final equilibrium position, corresponding with the passage of 18·4 fringes, but this equilibrium was attained so slowly that the investigators preferred to find it by extrapolation. The pressure producing flow was so small and the rate of descent of the disk so low (maximum $0·4\mu$ per sec.) that the air could be regarded as an incompressible fluid: the gradual reduction of the effective pressure owing to the flexure of the springs necessitated however some modification of the simple equation (VI. 4) in which F was supposed constant; a corrected equation is given by Brillouin.[11]

Experiments made to check Reynolds's equation have been described by Ormandy.[12] A transformer oil was used, in one arrangement, between a flat plate of glass and a plano-convex lens, the rate of settling of the lens with its plane face towards the flat being observed by means of interference fringes. Six of the observations agreed well with a curve given by

$$t = \text{constant} \times \{H_0^{-2} - (H_0 - x)^{-2}\},$$

where x is the distance travelled; irregularities of the surfaces caused the descent to become unduly slow when the film thickness was further reduced. In another arrangement, a flat disk of stainless steel 3 cm. in diameter was allowed to descend through a layer of oil towards a second disk, the distance between the surfaces being estimated from the capacity of the condenser former by the disks and the oil layer: the oil ceased to insulate the plates when the separation became reduced, after half an hour, to less than 15μ.

The experimental conditions are very much simplified, in the viscometer described by Michell,[13] by observing the separation instead of the approach of the surfaces. It is readily seen from equation (VI. 4) that in this case the time increases very slowly with the distance travelled after H has increased to some ten times its initial value: assuming that the same equation continues to

hold, the motion then becomes practically free from viscous constraint. If the force is that due to the action of gravity on the lower of two horizontal disks, this disk will appear to be at first attached to the upper one and to be released after a definite time, given by equating F to the weight of the disk and neglecting the term $1/H_0^2$ in comparison with $1/H_1^2$, where H_1 is now the initial separation. Instead of a flat disk, which would be liable to slide laterally instead of falling normally, Michell uses a steel sphere as the falling member: the sphere fits into a cup of suitable curvature, the distance between the surfaces being fixed by three pegs projecting radially inwards. The clearance is of the order of 0·01 mm. and may be varied in the manufacture to give instruments having different constants $k = t/\eta$.

The necessary modification of Reynolds's equation has been worked out by Boswall[14] for the cup-and-ball viscometer. For the special case in which the radii of the two surfaces are both equal to R, he finds

$$t = -\frac{9}{2}\frac{\eta R}{gCH^2}(2\log_e \cos\theta + \tan^2\theta), \quad . \quad . \quad (VI.\ 5)$$

where H is the initial film thickness, measured along the vertical axis, θ is the angle between the vertical axis and a radius drawn to the rim of the cup, and $C = 4\sigma - (2 + 3\cos\theta - \cos^3\theta)\rho$; the density of the material of the ball is σ and of the liquid ρ. A similar equation, with $\sin^2\theta$ instead of $\tan^2\theta$ in the bracket, holds for the special case in which the cup and ball are concentric: the general form—for the ball neither of equal radius nor concentric with the cup—is rather more complicated. Boswall states that a standard type of instrument has a sphere of one inch diameter with $\theta = 52°$, giving for the projected area of the film a circle of 1 cm. radius. He shows that deformation and temperature errors will produce minimum variations in the constant of the instrument if the projecting studs are disposed at a certain angle: for the special case of equal radii the studs should be at 45° from the vertical axis.

Some of the early models of the cup-and-ball viscometer were of such construction that the area of contact of the projecting studs with the sphere was by no means negligible compared with the total area of the cup. Under these conditions a considerable proportion of the resistance offered to the fall was due to the tenuous film included between the surfaces of the studs and the sphere.

This appears to have been the case in an example which was examined at the National Physical Laboratory in 1921 at the instance of the British Engineering Standards Association, for it was found that duplicate determinations might vary by $\pm$ 10 per cent. and that the intentional inclusion of air bubbles produced no effect on the time of fall; over a range of viscosities between 14 and 650 cp. the constant of the instrument varied from 43·9 to 40·6. Somewhat similar observations are recorded by Erk.[15] I am informed by Mr. Michell that in instruments made strictly to his own directions the studs are less than 1/16″ in diameter, instead of $\frac{1}{8}$″ as in this old model, and have convex surfaces so that the area of contact may be a minimum; with this construction it is possible to obtain satisfactory concordance between duplicate tests, the probable error of a single test being normally less than 1 per cent. Tests are now usually made by what used to be called the workshop method, the cup being first charged with a few drops of the oil under test and then pressed firmly, for about 1/3 of the expected fall time, on the ball, which rests on a clean board. The instrument is lifted up vertically by the insulated handle; a stop-watch is started at the same moment and is stopped when the ball falls off. The workshop instrument has a fairly substantial metal stem, in which a thermometer is inserted, but for laboratory purposes a model is supplied in which better thermal insulation of the cup from the operator's hand is secured by reducing the stem to a skeleton: in this sheath a glass tube is mounted, allowing the thermometer to be dipped into a pool of mercury placed inside the cup.

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THE TRANSPIRATION OF GASES

1. The capillary-tube method for a compressible fluid.
In the derivation of Poiseuille's Law (Chap. II, § 3) certain assumptions were made which are obviously unjustifiable in considering the flow of a gas along a tube. The known compressibility of gases leads us to expect that the velocity will increase from one end of the tube to the other, and we cannot therefore suppose the pressure gradient constant along the tube. Actually, the parabolic distribution of velocities across any section of the tube must be modified to some extent by the presence of a radial component, but Meyer[1] (1866) assumed that to a first approximation it was permissible to apply equation (II. 3) to the flow of gas through any given element of length of the tube if $-dp/dl$ were substituted for the P/l of that equation; thus,

$$Q = -\frac{\pi a^4}{8\eta} \cdot \frac{dp}{dl}$$

(neglecting the correction for slip at present). This simplification will involve the less error, the smaller the rate of change of density of the gas along the tube. Replacing Q, the volume rate of flow which is varying from one cross-section to another, by M, the mass rate of flow which is a constant, we obtain

$$M = \rho Q = -\frac{\pi a^4}{8\eta} \cdot \rho \frac{dp}{dl}, \quad . \quad . \quad . \quad \text{(VII. 1)}$$

where ρ is the density at the cross-section where the volume rate of flow is Q.

In integrating this equation it is assumed that η is constant, i.e. independent of the density: this was proved experimentally within certain limits by Maxwell[2] (1866). Meyer assumed also that Boyle's law holds, i.e. that the flow is isothermal and that the density is proportional to the absolute pressure: in that case

$$M = -\frac{\pi a^4}{8\eta l}\left(\frac{\rho}{p}\right)\int_{r_0}^{p_1} p \cdot dp$$

$$= \frac{\pi a^4}{16\eta l} \cdot \frac{\rho}{p}(p_0^2 - p_1^2), \quad . \quad . \quad . \quad \text{(VII. 2)}$$

where p_0 is the pressure at the entrance and p_1 that at the exit of the capillary.

The quantity of gas is normally determined by measurement of the change in volume in one or other of the two reservoirs in which the constant pressures p_0 and p_1 are maintained. If V_0 and V_1 are these volume changes, and t the time of flow,

$$V_0 p_0 = V_1 p_1 = \frac{\pi a^4 t}{16 \eta l}(p_0^2 - p_1^2). \quad . \quad . \quad \text{(VII. 2 a)}$$

When the velocity is high the assumption of isothermal flow is at least not obviously justifiable: Meyer himself recognized that equation (VII. 2) might lead to erroneous values for the viscosity if the pressure difference were large. Fisher[3] pointed out that equation (VII. 1) may also be integrated on the assumption that $\rho/p^{1/\gamma}$ is constant, instead of ρ/p, in which case equation (VII. 2) becomes

$$M = \frac{\pi a^4}{8 \eta l} \cdot \frac{\rho}{p^{1/\gamma}} \cdot \frac{\gamma}{\gamma+1}(p_0^{1+1/\gamma} - p_1^{1+1/\gamma}). \quad . \quad \text{(VII. 3)}$$

If the conditions are strictly adiabatic, γ is the ratio of the specific heat of the gas at constant pressure to that at constant volume, and may reach the value 1·66 for a monatomic gas. For conditions intermediate between adiabatic and isothermal we may assign some arbitrary value n to this coefficient: with $n = 1$ equations (VII. 2) and (VII. 3) become identical.

Trautz and Weizel[4] have discussed at some length the applicability of Fisher's formula, which would lead to values for the viscosity about 4 per cent. lower than are indicated by Meyer's equation for their experimental conditions ($p_0 = 950$ mm., $p_1 = 760$ mm. of mercury, $\gamma = 1\cdot4$). They show that the work done against viscous forces in the capillary supplies a large proportion of the heat required to make the flow isothermal: their calculations indicate that Meyer's equation may be used without error, at any rate for temperatures between 0° C. and 100° C.

The same authors have developed a correction for the deviations from Boyle's Law which become important for readily liquefiable gases or for vapours. Adapting the method indicated by them, we combine the a and b terms of van der Waals's equation in the approximate solution $\rho/\{p(1 - Cp)\} = RT = \text{constant}$, where $C = b/RT - a/(RT)^2$. By introducing this relation into (VII. 1) we obtain on integration

$$M = \frac{\pi a^4}{8 \eta l} \cdot \frac{\rho}{p(1 - Cp)} \left\{ \frac{p_0^2 - p_1^2}{2} - \frac{C(p_0^3 - p_1^3)}{3} \right\}. \quad \text{(VII. 4)}$$

No rigid solution has yet been given for the problem of the quasi-streamline flow of a compressible viscous fluid in a tube: such a solution would need to take into account not only the acceleration of the fluid in the axial direction but also the radial flow.

2. The kinetic-energy correction. Although the need for the application of the Hagenbach correction was early recognized in connexion with determinations of the viscosity of liquids and there had been considerable discussion as to the precise value of the coefficient m (Chap. II, § 4) before the close of the last century, it was pointed out by Brillouin in 1907 that no investigator working with gases had made any such correction. As in the deduction of Hagenbach's correction, Brillouin[5] found that the kinetic energy of the emergent jet corresponded with a fall in pressure,

$$\delta p_1 = \frac{\rho_1}{\pi^2 a^4}\left(\frac{M}{\rho_1}\right)^2.$$

Introduction of this value into Meyer's equation (VII. 2) gives, if δp_1 be small,

$$\eta = \frac{\rho}{p}\frac{(p_0{}^2 - p_1{}^2)\pi a^4}{16\,Ml} - \frac{M}{8\pi l} \quad . \quad . \quad . \quad \text{(VII. 5)}$$

Although the densities of gases are very low compared with those of liquids, the kinetic-energy correction is usually of some importance since the linear velocities tend to be much higher in measurements of the viscosity of gases.

Criticisms of Brillouin's formula were advanced by Fisher,[3] who then deduced a correction[6] by a different method. Application of Bernoulli's equation to the conditions at the entrance, where the average of the squares of the velocities is $(\bar{u})^2$, gives

$$RT\log_e(p_0/p_0') = -\tfrac{1}{2}(\bar{u})^2,$$

if it is assumed that the expansion is isothermal; in this expression p_0' is the pressure measured in the reservoir and p_0 that just inside the capillary. Substituting the value of $(\bar{u})^2$ found from Meyer's formula, he obtained

$$RT\log_e\frac{p_0'}{p_0} = \frac{a^4}{384}\left(\frac{p_0^2 - p_1^2}{\eta p_0 l}\right)^2 . \quad . \quad . \quad \text{(VII. 6)}$$

A similar expression, with subscripts $_1$ in the logarithmic term on the left and in the denominator on the right, gives the ratio of the pressures for the exit end.

If the correction is small we may write Fisher's two equations, after expanding the logarithms, in the approximate form

$p' - p = k/p$, where $k = \dfrac{\rho}{p} \cdot \dfrac{a^4}{384}\left(\dfrac{p_0^2 - p_1^2}{\eta l}\right)^2$. Substituting for η by

equation (VII. 2), it will be seen that the pressure-drop at the entrance amounts to $\frac{2}{3} M^2/(\rho_0 \pi^2 a^4)$. The pressure in the exit end of the capillary is less than the static pressure beyond it by an amount equal to two-thirds of that given by Brillouin. Taking note of the signs, the net resultant change in $(p_0^2 - p_1^2)$ differs from zero only by a quantity which is of a second order of smallness, but is of opposite sign to that indicated by (VII. 5).

Benton[7] has criticized Fisher's formula in that it leads to the result that when the driving pressure is large the mass discharge should decrease as the pressure difference increases. His own experimental results, obtained under conditions such that the kinetic-energy correction was large, were in fair agreement with Brillouin's formula (VII. 5), but suggested that the correction term should be multiplied by a coefficient C, greater than unity and probably varying with the radius and with the pressure gradient. The mean value of this coefficient deduced from his empirical formula is 1·215. Since the capillaries used by Benton had sharp edges, he ascribed the increase to a *vena contracta* effect, C being the ratio of the radius of the tube to that of the minimum cross-section of the jet of gas. No author appears to have recognized that the calculations of Boussinesq and of Schiller (Chap. II, § 4) should be applicable, at least in first approximation, to the conditions at the inlet end of a tube through which gas is flowing: there is little reason to doubt that Benton's coefficient C may be identified with the m of Chapter II and that it is subject to similar variations.

Fisher's argument is entirely analogous to that advanced by Grüneisen and by Applebey for liquids, according to which the loss of head due to the kinetic energy imparted to the liquid at the inlet is entirely recovered by the lowering of the pressure in the emergent jet below the static pressure of the recipient reservoir. This reasoning holds good only if the flow is so slow, or the change of cross-section at the end of the capillary so gradual, that there is no turbulence in the down-stream reservoir: in these circumstances, the work of Bond and of Dorsey (Chap. II, § 6 (e))

indicates $m = 0$ for liquids; the small correction obtained by Fisher is due to energy assumed to have been supplied as heat from the walls of the tube to make the flow isothermal. In general, and particularly at the relatively high Reynolds's numbers usually encountered in determinations of the viscosity of gases, m is not zero but approaches the value 1·1, the energy of the issuing jet being dissipated in viscous work *outside* the capillary. It may be remarked that though Fisher assumed isothermal conditions throughout, the flow would probably be more nearly adiabatic at the actual ends, particularly at the exit.

Trautz and Weizel[4] made determinations of the end-correction by means of the familiar device of subdividing a tube and observing the increase of resistance. Their conditions were such that the correction was small, but their results were in satisfactory agreement with a formula requiring the loss of head to be proportional to kinetic energy only: they found that no other end correction was necessary, e.g. the requirement $l/2a > 3000$, proposed by Meyer, was superfluous. Analytically they deduced a formula which is almost equivalent to that of Brillouin, but they added to the pressure-drop at the inlet a further pressure-drop calculated to allow for the acceleration of the gas at each point along the tube. Their final value for the correction is greater than Brillouin's in the ratio $(2p_0 - p_1) : p_1$. By stating their differential equation a little more elaborately it is found, however, that the increase in the correction is equivalent to that due to the work done in the assumed isothermal expansion of the gas as it flows along the tube. Since this energy is supposed to be supplied by conduction through the walls there is no valid reason for adding it to the kinetic-energy term.

Summarizing, the available experimental and theoretical results appear to lead to a kinetic-energy correction identical with that obtained for liquids. If Meyer's equation may be assumed to hold for parts of the tube remote from the ends, equation (VII. 5) gives the value of η in terms of the pressures measured at the ends of the tube, except that the correction $M/(8\pi l)$ should be multiplied by a coefficient m, of which the normal value is probably 1·1. In the viscometry of gases conditions should be selected so that the kinetic-energy correction is small, not only to avoid error due to the use of a possibly erroneous value of the coefficient, but also to render the assumption of isothermal flow most probable.

3. Correction for slip. In dealing with liquids we have assumed that there is no slip at the walls, i.e. that the layer of liquid in contact with the walls of a capillary tube remains at rest when liquid flows through the tube. The evidence available shows that this assumption is correct within the accuracy of the experimental methods available for the detection of the results of slip of liquids. In the case of gases there is very strong evidence to show that something occurs which may be interpreted as slip. One of the simple consequences of the kinetic theory proposed by Clausius (1857) is that the viscosity of a gas should be independent of pressure: the confirmation of this deduction by Maxwell, over a range of pressures from 9·5 in. to 30 in. of mercury, did much to establish the theory. At 'low' pressures, however, Kundt and Warburg (1875) found that the logarithmic decrement of their oscillating disk (cf. Chap. IX, § B IV) was no longer constant: their results showed that a definite decrease occurred when the mean free path of the gas, calculated from the viscosity by application of the kinetic theory, became comparable with the thickness of the layer subjected to shear. Experiments on flow through capillaries are not so well adapted to the determination of this effect, but measurements by Warburg (1876) and by Knudsen[8] show that the resistance offered by a tube decreases at low pressures. The data may be interpreted as indicating that the gas 'slips' along the wall at the same rate as it would move, in the absence of slip, if the surface at which there was complete adhesion lay a distance λ beyond the wall. Meyer showed in his *Kinetic Theory of Gases* that within the limit of experimental error λ might be taken as equal to the mean free path. The elementary kinetic theory gives the mean free path as

$$L = \sqrt{\left(\frac{3}{p\rho}\right)}.$$

It has been pointed out by Williams[9] that the ratio between the slip coefficient and the mean free path varies between 0·85 and 1·41, depending on the particular formulation adopted for the distribution of molecular velocities: he prefers therefore to calculate the value of λ from Knudsen's semi-empirical equation

$$\lambda = 0\cdot81 \cdot \frac{8\eta}{3} \cdot \sqrt{\frac{2}{\pi p\rho}}.$$

If in deriving the Poiseuille Law (Chap. II, § 3) we put $u = 0$

at $r = a + \lambda$, the resulting expression for the volume flowing per second is modified by the substitution of $a^4\left(1 + 4\dfrac{\lambda}{a}\right)$ for the a^4 of equation (II. 3). When λ is assumed to have a constant mean value along the tube, the same factor appears in Meyer's equations (VII. 1 and 2); since λ varies inversely as the pressure it becomes necessary to decide on a mean value. Warburg suggested a method of calculation which Bestelmeyer[10] showed to be erroneous, owing to neglect of the effect of compressibility: the correct equation is

$$M = \frac{\pi a^4}{8\eta l}\,\frac{\rho}{p}\,\frac{p_0^2 - p_1^2}{2}\left(1 + 4\frac{\lambda_m}{a}\right), \qquad . \quad . \quad \text{(VII. 7)}$$

where λ_m is the mean free path corresponding with the average pressure $\frac{1}{2}(p_0 + p_1)$. For pure gases, values of λ_m may be deduced from those of λ_0, the mean free path at N. T. P. given in tables of constants: for a mixture of gases a close approximation may be deduced, after a first estimate of the viscosity has been obtained, from the relation (Rankine[11])

$$\frac{\lambda}{\lambda_s} = \frac{\eta}{\eta_s}\sqrt{\frac{\rho_s}{\rho}}\,,$$

where λ, η, and ρ refer to the mixture and λ_s, η_s, and ρ_s to a standard gas at the same pressure.

4. The capillary. The viscosities of gases vary over a much smaller range than those of liquids and have smaller temperature-coefficients: one capillary will therefore serve for measurements on any gas. Although the kinematic viscosities are not small—that of air is some 15 times that of water at room temperatures—the driving pressures are usually measured in terms of a column of liquid, as in the viscometry of liquids. In order to secure a low rate of flow it is therefore necessary to make use of a capillary of very small bore: radii as small as 0·05 mm. have been selected for measurements in which the driving pressures were provided by columns of mercury. The calibration of these fine capillaries is therefore normally more difficult than that of tubes to be used for liquids, but can only be carried out by similar methods. The procedure adopted by Schultze[12], which has been frequently quoted, is substantially that described in Chap. III, § 2, A (2); the value of L/a^4 is taken as $\sum_0^L (l/r^4) = \dfrac{\pi^4}{v^2}\sum_0^L (\lambda^2 l)$, where $V/v = \sum_{l_1}^{l_2}(l/\lambda)$, λ is the length and r the mean radius of a mercury column whose

centre is moved by successive equal distances l along the tube, and v is the volume of the calibrating thread determined from the volume V of a long thread of length $(l_2 - l_1)$. Fisher's method[13] is now preferred. Experimentally it is identical with Schultze's, but the summations are replaced by graphical integrations: assuming Meyer's equation, Fisher writes for any cross-section of the tube

$$\frac{d\,(p^2)}{dl} = \frac{\text{constant}}{r^4} = \frac{k\pi^2\lambda^2}{v^2},$$

whence

$$p_0^2 - p_1^2 = k \int_0^L \frac{dl}{r^4} = \frac{k\pi^2}{v^2} \int_0^L \lambda^2 \,.\, dl.$$

The integral is evaluated by plotting λ^2 against the distance of the mid-point of the thread from the zero mark and finding the area bounded by the curve and the axes. Similarly, the volume v of the pellet is obtained by plotting $1/\lambda$ against the above distance, evaluating the integral between the cross-sections at l_1 and l_2 and putting

$$V/v = \int_{l_1}^{l_2} \frac{dl}{\lambda}.$$

If the calibration is sufficiently detailed the two methods of computation yield the same result, even when the irregularity of the tube is such that calculation of the mean radius directly from the mass of mercury which fills the tube gives a value for the viscosity too high by 1·5 per cent. (Rapp[14]).

5. Apparatus. It will be impossible—and it is probably unnecessary—to give detailed descriptions of the numerous forms of apparatus which have been constructed for the measurement of the viscosity of gases by the transpiration method. A conspectus is given below of the types adopted by various workers: a description of a few forms will follow.

I. Volume of a large reservoir fixed.

(a) Rise of pressure p_1 observed in down-stream recipient, nearly vacuous (Graham, 1846) or about one-third evacuated; p_0 atmospheric or regulated to constancy by a supply of gas to an up-stream reservoir (Graham).

(b) Fall of pressure p_0 observed in up-stream reservoir: p_1 atmospheric (Graham).

(c) Meyer (1873) observed the simultaneous changes of p_0 in a large reservoir up-stream and of p_1 in a large reservoir down-stream.

II. Pressure difference, fixed by construction of apparatus, varying during an experiment, p_1 atmospheric: volume from preliminary integration of $p_0 \, dV/(p_0^2 - p_1^2)$ (Trautz and Weizel, 1925).

III. Pressure difference $(p_0 - p_1)$ maintained constant by regulation of the supply or withdrawal of liquid:

(a) Volume V_0 measured: p_1 is approximately zero (Graham) or atmospheric (Wiedemann, 1876, Breitenbach, 1899, Roberts, 1912) or is continuously regulated, by hand, to any desired value (Schultze, 1901, Piwnikiewicz, 1913).

(b) Volume V_1 measured: p_0 is atmospheric, p_1 being regulated automatically (Meyer, Obermayer, 1877) or by hand (Rapp, 1913).

(c) In one form of apparatus Meyer made measurements by both methods (a) and (b).

Type I. In the measurements of type I it is not possible to use formula (VII. 2a), which was derived on the assumption that the flow was uniform: if the rate of change of pressure is small and the velocity low, equation (VII. 2) may, however, be applied to give the mass rate of discharge at any instant. If p_0 is constant we may then write

$$p_0^2 - p_1^2 = kV_1' \frac{dp_1}{dt},$$

where $k = 16 \, \eta l/(\pi a^4) = $ a constant for a given gas and a given capillary and V_1' is the constant volume of the recipient. Integrating between the limits 0 to t and p_1 to p_1', we obtain

$$t = \frac{kV_1'}{2 \, p_0} \log_e \left(\frac{p_0 + p_1'}{p_0 + p_1} \cdot \frac{p_0 - p_1}{p_0 - p_1'} \right). \quad . \quad . \quad \text{(VII. 8)}$$

This equation was derived by Meyer and applied to Graham's observations of the times corresponding with certain changes of pressure.

For Meyer's own experiments (I c above) in which V_0' and V_1' were fixed, so that both p_0 and p_1 varied, a similar treatment gives

$$t = \frac{kV_0'V_1'}{2 \, (V_0'p_0 + V_1'p_1)} \log_e \left(\frac{p_0' + p_1'}{p_0 + p_1} \cdot \frac{p_0 - p_1}{p_0' - p_1'} \right). \quad \text{(VII. 8 a)}$$

Apparatus of this type is not well adapted to the accurate measurement of viscosity, owing to the relatively large volume of gas which has to be maintained at constant temperature. Further, the capillary requires to be small enough to ensure a negligible

kinetic-energy correction at the beginning of an experiment, when the pressure difference is greatest; its mean radius is therefore liable to be less accurately determined than in apparatus of type III in which low driving pressures and wider capillaries may be used.

Type II. The principle adopted by Trautz and Weizel[4] leads to simplicity not only in construction but also in operation and observation. Essentially the apparatus (Fig. 30) consists of two bulbs, an upper one of 200 cm.³ and a lower one of 250 cm.³ joined by a wide-bore U-tube, the capillary being connected by a three-way cock to the lower bulb. A fixed volume of mercury is introduced, sufficient to fill the lower bulb and nearly half of the upper bulb: the gas is caused to displace mercury from the lower bulb into and above the upper bulb. On turning the cock to allow the gas to flow through the capillary into the atmosphere, the higher mercury-level falls until it reaches a graduation mark m_1 on the tubing just above the upper bulb: at this moment a stop-watch is started, which is stopped when the rising meniscus in the lower bulb reaches another mark m_2 placed on the 5 mm. bore tubing which leads to the stop-cock. So long as the positions of the bulbs and the quantity of mercury remain unchanged, the time recorded is that required for a definite quantity of gas to be

FIG. 30. Method of Trautz and Weizel (after the figure in *Annalen der Physik*).

driven through the capillary under a definite head. The apparatus is more suitable for relative than for absolute measurements. Trautz and Weizel, however, made their values absolute by determining the volumes of gas which were present in the lower bulb when the mercury was at different levels: for this calibration a gas-burette and a manometer were temporarily attached. The volumes V were plotted against the pressure excesses $(p - p_1)$ read on the manometer: from this curve another was constructed showing $p/(p^2 - p_1^2)$ as a function of V, and the area enclosed by this

curve between the initial and final values p_a and p_e of the pressure gave the value of the integral of $p\,dV/(p^2 - p_1^2)$. Then

$$\int_{p_a}^{p_e} \frac{p\,dV}{p^2 - p_1^2} = \frac{\pi a^4 t}{8\,\eta l} \cdot \quad . \quad . \quad . \quad . \quad \text{(VII. 9)}$$

If the temperature θ of the capillary is different from that of the measuring bulb θ_0, the integral requires to be multiplied by θ/θ_0: corrections are applied for variations of the atmospheric pressure p_1 from the standard and for the effect of temperature on different parts of the apparatus. Most of the corrections require for their evaluation a graphical method for which the original paper should be consulted.

Type III. Most of the more recent determinations of the viscosities of gases have been made by means of apparatus of the third type, form (*a*) being preferred when the quantities of gas available are small and form (*b*) when the gas examined is one such as air, of which there is an unlimited supply.

Rapp's apparatus[14] may be described as an example of type III b. It consists (see Fig. 31) of a bottle, provided with a siphon H and manometer O, into which gas is aspirated through the capillary D. The gas—dry air in Rapp's experiments—is supplied at atmospheric pressure at A, escaping continually through B: it is brought to the temperature of the capillary during its passage through the wide tubing C. Transformer oil contained in the bottle siphons into the bucket K, which has an overflow tube at the level N: the rate of discharge of oil, which depends on the difference in level MN between the surfaces in the bottle and in the bucket, and on the pressure indicated by the manometer O, is kept constant by lowering the bucket by means of a micrometer screw *pari passu* with the fall of the oil-level in the bottle, so that the manometer reading remains steady. The volume-rate of flow of gas through D, measured at the temperature and pressure prevailing in the bottle, is then equal to the volume of oil overflowing from K in a measured time: this oil is collected and weighed. The density of the oil at the temperature of the bath must be determined accurately, since this value affects the driving pressure $(p_0 - p_1)$, the volume V_1, and the pressure p_1 under which this volume of gas is measured. To the volume of oil collected there must be added a volume equal to the cross-section of the siphon-tube multiplied by the distance through which the bucket is lowered.

The capillaries used by Rapp had radii 0·056 to 0·251 mm., lengths 0·5 to 1·0 metres: with driving pressures equivalent to from 6·3 to 24·5 cm. of mercury, volumes of 0·4 to 1·1 litres were collected in times which varied from 280 to 7,200 seconds. In long runs it was necessary to correct for the effect of variations of barometric pressure between the beginning and end of an experi-
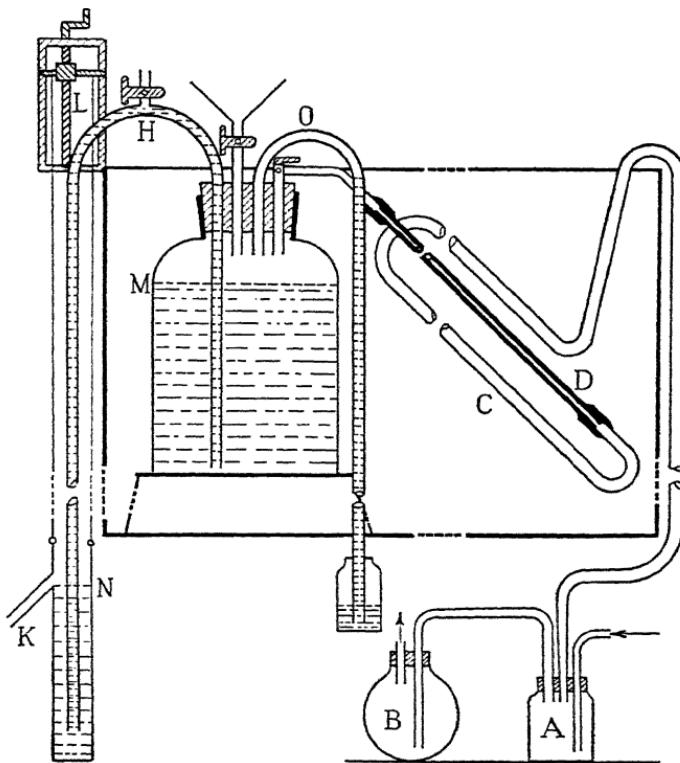
FIG. 31. Rapp's apparatus (after the figure in *Physical Review*).

ment. It may be noted that it is essential, in this method, to maintain the manometric pressure as constant as possible, since a correction for any variation in pressure during an experiment would be extremely troublesome to apply. Fisher,[13] in a somewhat similar type of apparatus, used a motor to lower the bucket at a uniform rate: Rapp found it possible to regulate the descent by hand so that the head remained constant to 0·5 mm. on a minimum oil column of 100 cm.

The use of oil in the aspirator avoids corrections for the pressure

of water vapour which were necessary in Meyer's earlier form. Gases—including air—are, however, somewhat soluble in oil, though the rate of solution is less than in water: when the solubility is likely to cause error, mercury must be used. When the supply of gas is limited, Fisher's modification[13] of Schultze's apparatus may be adopted, in which the pressure is regulated in both an up-stream and a down-stream reservoir. Trautz and Weizel[4] have shown that, when the capillary is maintained at temperatures far from atmospheric, only moderate lengths of heating coil (as C in Fig. 31) are required to ensure thermal equilibrium.

6. Rankine's method. A considerable number of measurements have been made in recent years by an ingenious method of which the principle appears to have been first applied by Pedersen[15] though the development of the apparatus and theory are due to Rankine.[16] In its simplest form the apparatus consists of a capillary and a 'fall-tube' sealed at each end to a Y-tube to produce a closed system. A pellet of mercury falling vertically down the wider tube drives gas from the bottom to the top of the capillary: the weight of the pellet and the diameter of the fall-tube being known, the time of fall of mercury between two marks gives the volume-rate of flow of the gas through the capillary under a constant pressure-difference. The apparatus is so mounted that the direction of travel of the mercury may be reversed, after the lower mark has been reached, by rotating the system about a horizontal axis, care being taken that the fall-tube becomes vertical in each position.

The mathematical examination of the conditions of the flow of the gas is complicated by the fact that the pressures in the fall-tube above and below the pellet are functions of the position of the mercury. Rankine shows, however, that making the restrictions (i) that the pressure difference p due to the pellet is negligible compared with the total pressure P prevailing in the apparatus, and (ii) that the volume v swept out by the tail of the pellet is symmetrically placed with respect to the ends of the capillary,

$$\eta = \frac{\pi a^4 p t}{8 l v}; \quad . \quad . \quad . \quad . \quad \text{(VII. 10)}$$

where a is the radius and l the length of the capillary and t is the time required for the tail of the pellet to pass from one mark to

the other. A first approximation to the modification required in the formula if the stated restrictions are not obeyed is obtained by multiplying v by the factor

$$\left\{1 - \frac{1}{12}\left(\frac{pv}{PV}\right)^2 + \frac{p\,\alpha}{2\,PV}\right\},$$

where V is the total volume not occupied by the mercury and α is the excess of the volume above the upper mark over that below the lower mark. With $p = 5$ cm. and $P = 75$ cm. of mercury, the second term of this factor is less than $1/3000$; with $\alpha = V/7$ the third term amounts to 0·5 per cent., but if the mean of the times of fall in the two directions is taken as t in formula (VII. 10) the error in η will not reach 0·1 per cent. until $\alpha = \frac{2}{3}V$.

The pressure difference p is not exactly equal to the weight mg of the mercury divided by the area of cross-section A of the fall-tube. The upper surface of the falling pellet may be seen to be much less curved than the lower surface: hence the effects of capillarity are not equal and opposite, but their resultant tends to retard the fall. In his earlier experiments Rankine obtained an estimate of the reduction in pressure due to surface tension by introducing mercury pellets of different weights and timing their fall, but a more convenient method was indicated by Kuenen and Visser[17] which avoids the necessity for opening the tube. In their procedure a constant mass of mercury is used and times are observed when this mass falls as one, two, or more pellets. By plotting $1/t$ against the number n of drops used they found that the relation was approximately linear, at any rate until the pellets had been several times subdivided; thus $p = mg/A - nc = b/t$, where b and c are constants. Extrapolation to $n = 0$ gives a value b/t_0 which indicates the time which would have been required if there had been no surface effects: for pt in equation (VII. 10) we may therefore substitute mgt_0/A.

The reduction of driving pressure due to capillarity has been studied by Rankine and Smith,[18] using the method of Kuenen and Visser. They find that the effect varies considerably with the temperature and slightly with the nature of the gas with which the mercury is in contact: further, the relation between $1/t$ and n is strictly linear for segments longer than 15 mm. (in a 3 mm. fall-tube). Hence it is sufficient to observe the times t_1 and t_3 for the same volume of gas to be displaced when the pellet is first intact

and then in two parts, and to calculate the ideal time t_0 corresponding with a driving pressure mg/A as

$$t_0 = t_1 t_2/(2 t_2 - t_1). \quad . \quad . \quad . \quad \text{(VII. 10 a)}$$

Rankine made some absolute measurements with his first apparatus (1910) which agreed within $\frac{1}{2}$ per cent. with those of other observers. On account of the very small bore needed for the capillary, which militates against accurate determination of a^4, the method is more suitable for relative measurements, in which the viscosity of air may be taken as standard. For such purposes the smallness of the quantity of gas required is frequently an advantage, but Rankine does not recommend the use of the apparatus at temperatures higher than 100° C. owing to the increasing vapour pressure of the mercury. Introducing the correction for slip, which may be necessary when the mean free path of the gas differs considerably from that of air, the expression for the relative viscosity becomes

$$\frac{\eta}{\eta_s} = \frac{t}{t_s} \cdot \frac{1 + 4\lambda/a}{1 + 4\lambda_s/a}$$
$$= \frac{t}{t_s} \left\{ 1 + 4\frac{\lambda_s}{a}\left(\frac{\lambda}{\lambda_s} - 1\right) \right\}, \quad . \quad . \quad \text{(VII. 10 b)}$$

where η_s, t_s, and λ_s refer to the standard gas. Both t and t_s are corrected times, obtained from measurements with a divided and with an intact pellet.

A useful *résumé* of the theory and some practical details of the construction and manipulation of the instrument are given by Rankine.[19] He recommends that the capillary be some 50 cm. in length and 0·2 mm. in diameter, that the bore of the fall-tube be between 3 and 3·5 mm. and that the marks A and B (Fig. 32) be about 30 cm. apart. The bulbs CC, of about 1 cm. diameter, serve to accommodate the mercury while the apparatus is being evacuated. Kuenen and Visser placed slight constrictions at the junctions of the fall-tube with the bulb to facilitate the divisions of the pellet, though Rankine does not regard them as necessary. The stop-cocks TT are in tubing of about 1 mm. bore. The viscometer is mounted in a wide tube through which steam may be blown if required and the whole is so clamped that it may be rotated through 180° about a horizontal axis.

The chief difficulty in the use of the apparatus is in the thorough cleaning and drying which is necessary at intervals. Since the

capillary and fall-tube are in parallel, the flow of solvents and of currents of dry air through the former is necessarily very slow. If cleaning liquids in the capillary become divided into several short columns, they can be dislodged only with difficulty: I have noticed that such columns form very readily during the cleaning if the capillary is bent twice through 180°, as suggested by Rankine in order to furnish a greater length in a shorter apparatus. Repeated evacuation and refilling with dry air at 100°C. is the easiest method of completing the drying. The stop-cocks should not, however, be greased until after the pure mercury, sufficient to form a pellet about 4 to 5 cm. in length, has been introduced into the bulbs. If the mercury happens to enter the capillary, its removal may be extremely troublesome. The same quantity of mercury will serve for a large number of observations if the glass is thoroughly dry and the mercury very pure, provided that the gases which are examined are both dry and non-corrosive: it is advisable to leave the mercury in the bulbs rather than in the fall-tube when the apparatus is idle. Cleaning is necessary

FIG. 32. Rankine's gas viscometer (after the figure in *Journal of Scientific Instruments*).

whenever the descent of the pellet is observed to become irregular, the angle of contact between the mercury and the glass appearing to vary.

It is possible to obtain measurements of the viscosity of gases such as sulphuretted hydrogen or coal-gas if observations are made rapidly, (i) with pellet intact, (ii) with pellet divided, (iii) with pellet intact, the mean of the times (i) and (iii) being taken as t_1.

The apparatus will require cleaning after use with such gases : a modification adapted for the examination of corrosive gases has been described by Rankine,[20] in which a cushion of air is inserted between the fall-tube and the capillary by means of a tube which may be swept out with air after each observation.

7. The viscosity of vapours. The capillary tube method is not usually the most suitable for the determination of the viscosity of vapours. At mean pressures approaching the saturation pressure, adsorption (or even accidental condensation) of vapour on the walls may produce error in the estimated effective resistance of the capillary; further, the equation of state, which needs to be introduced into the calculation (cf. § 1), is not always known with the required accuracy. At lower pressures the mass rate of flow corresponding with the linear velocities permitted by Reynolds's criterion becomes inordinately slow, since the viscosity is practically independent of the pressure: the rate of transpiration has usually been obtained by condensing the vapour to a liquid, of which the weight or volume is determined; this procedure requires the flow of a large volume of vapour.

We shall not therefore describe the apparatus used by Meyer (1879) and Schumann (1881) for the measurement of the viscosity of vapours, which is of little more than historical importance. A method due to Rankine,[21] though by no means generally applicable, merits some consideration, however, in view of the simplicity of its design and operation. In this method (see Fig. 33) the driving pressure is obtained from the difference between the saturation pressures of the liquid in two U-tubes maintained at different constant temperatures lower than that, of the capillary, at which the viscosity is to be measured. The limbs of the U-tube are graduated in millimetres and carefully calibrated for volume. For experiments with bromine vapour from room temperature to 220° C., Rankine used a 39 cm. capillary of about 1/3 mm. bore; the U-tubes, of 2 mm. bore, had limbs 20 cm. long and were immersed one in ice and the other in water just below the temperature of the air. The apparatus was temporarily connected to a suitable pumping system, the liquid was introduced and all air removed: the lead to the pump was then sealed off. When the temperatures of the three baths had been adjusted, observations were taken of the four liquid levels at intervals.

The pressures in the closed limbs of the U-tubes are assumed to be the saturation pressures at the respective temperatures. Slightly different pressures prevail in the limbs which are connected to the capillary, owing to the fact that heat does not pass through the walls fast enough to supply—or to dissipate—the latent heat of evaporation or condensation. The pressures p_0 and p_1 at the ends of the capillary are therefore equal to the saturation pressures corresponding with the temperatures of the U-tube baths *minus*—or *plus*—the pressure differences indicated by the
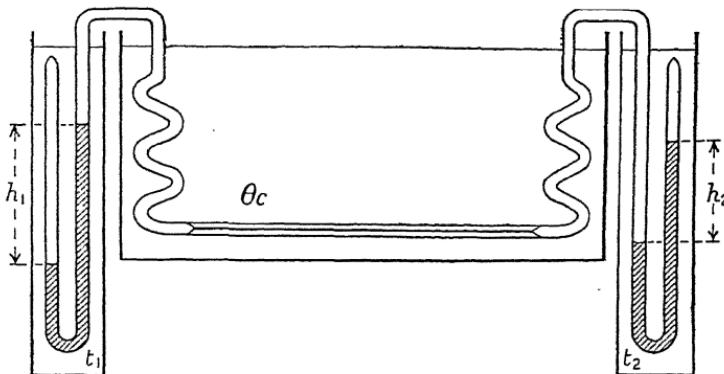
FIG. 33. Rankine's vapour viscometer (after the figure in *Proceedings of the Royal Society*).

levels of the liquid. The mass of vapour which has flowed through the capillary in a given time may be obtained from the fall of the levels in the warmer U-tube if the density of the liquid is known. If the capillary is at an absolute temperature θ_c, Meyer's formula (VII. 2) becomes

$$\eta = \frac{\pi a^4}{16 l} \cdot \frac{p_0{}^2 - p_1{}^2}{M} \frac{\rho \theta}{p \theta_c}, \quad \cdot \quad \cdot \quad \cdot \quad \text{(VII. 11)}$$

where the density ρ of the vapour at normal temperature θ and pressure p may be calculated from the molecular weight. In Rankine's experiments the average pressure was only about 10 cm. of mercury and Boyle's Law appeared to hold accurately; the slip correction varied from 0·5 to 2·0 per cent. at different temperatures.

Slight modifications of Rankine's vapour viscometer are described by Smith[22] and by Nasini.[23]

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(23) Nasini, *ibid.*, 1929, **123 A,** 692, 704.

THE FALLING-SPHERE METHOD

1. Stokes's Law. If a body is acted upon by a constant force and the resistance to its motion is proportional to the velocity or to any power of the velocity, the body will eventually attain a constant or terminal velocity such that the resistance experienced is equal and opposite to the driving force. The enunciation of this fact is due to Newton,[1] but its detailed application to physical problems is comparatively recent. The classical equations of hydrodynamics, propounded by Poisson, Navier and others, were first solved by Stokes[2] for the case of a pendulum having a spherical bob oscillating in a viscous fluid. In particular, for a pendulum having an infinite time of swing, i.e. for a sphere moving with uniform velocity, he evaluated the resistance to the motion as

$$W = 6\pi\eta av, \quad . \quad . \quad . \quad \text{(VIII. 1)}$$

where a is the radius of the sphere and v its constant velocity. The mathematical treatment will be found, e.g., in Lamb's *Hydrodynamics*.[3] The solution applies only to low velocities and is a first approximation only, being obtained by neglecting, in the equations of motion of the fluid, all terms of the form $\rho u \dfrac{\partial u}{\partial x}$, the so-called 'semi-quadratic' terms, which are assumed to vanish in comparison with the terms of the form $\eta \Delta u$. Consideration of the relative orders of magnitude of the respective terms led Rayleigh[4] to point out that this assumption is only warranted if $va\rho/\eta$ be negligible compared with unity.

If equation (VIII. 1) be applied to the case of a sphere falling under the action of gravity in a viscous medium, we may obviously equate W to the apparent weight of the sphere when equilibrium has been attained, since there is then no acceleration; this gives

$$\frac{4}{3}\pi a^3 (\sigma-\rho) g = 6\pi\eta av,$$

or
$$\eta = \frac{2}{9}\frac{(\sigma-\rho)g}{v} a^2. \quad . \quad . \quad . \quad \text{(VIII. 2)}$$

Here, and throughout this chapter, σ denotes the density of the sphere, ρ that of the fluid: as usual, g represents the acceleration due to gravity.

We shall refer to this equation as Stokes's Law, and to the hydrodynamical equations from which it is derived and in which the inertia terms are ignored, as Stokes's system of equations.

Though we are here concerned with the use of equation (VIII. 2) as a means of determining the viscosity of a fluid from the velocity with which a sphere of known radius falls therein, it may be remarked that this has not hitherto been the most important application of Stokes's Law. The law has been widely used, conversely, in estimating the size of a small sphere from its rate of fall: it has been made to provide, for instance, determinations of the diameter of droplets of water in the mists or fogs occurring in nature or produced artificially, and it affords in many cases the only practicable method of finding the dimensions of microscopic particles, e.g. in sedimentation analysis.

2. Oseen's correction. Many attempts have been made to deduce a closer approximation than is given by Stokes's Law, by taking into account some of the terms which are assumed to be negligible in the development of the law from his system of equations. A critical account of these attempts may be found in a paper by Weyssenhoff,[5] but discussion of them may be omitted here since they led to no improvement. It is not until the original differential equations are stated more accurately that it becomes possible to find a second approximation.

It was pointed out by Oseen[6] that it is only in the immediate neighbourhood of the moving body that the semi-quadratic terms may be neglected in comparison with those expressing the viscous forces, and that at a great distance from the sphere (or cylinder) they become actually the more important. For the case of the sphere Oseen showed that the distribution of fluid velocities deduced when the 'semi-quadratic' terms are included was essentially different from that found by Stokes, that in front of the sphere being no longer a mirror image of that behind it. Actually so long as the Reynolds's number R ($= vd\rho/\eta$) is negligibly small compared with unity, the resistance offered to the sphere agrees with that given by equation (VIII. 1) above, but a closer approximation is obtained at higher speeds by the modified form

$$W = 6\pi\eta av\left(1 + \frac{3}{16} R\right). \quad . \quad . \quad \text{(VIII. 3)}$$

In the derivation of this formula Oseen assumes[7] that R^2 is

negligible compared with unity. An exact solution of Oseen's system of equations, no longer involving this assumption, has recently been given by Goldstein.[8] Up to $R = 2$ the solution takes the form of a series with ascending powers of R; for higher values, up to $R = 20$, the equations are solved by numerical computation. The difference from Oseen's result amounts to 0·05 per cent. at $R = 0·2$, to 1·0 per cent. at $R = 1$, to 3·1 per cent. at $R = 2$ and to 10 per cent. at $R = 5$, the resistance increasing less rapidly than is indicated by (VIII. 3).

Stokes's approximation leads to a curious paradox when his system of equations is applied to the movement of an infinite cylinder in an infinite medium, the only stable condition being that in which the whole of the fluid, even at infinity, moves with the same velocity as the cylinder. The paradox is removed when the inertia terms are no longer entirely neglected.

3. Limiting speed for Stokes's or Oseen's Law. Strictly speaking, it is impossible to discriminate experimentally between equations (VIII. 1) and (VIII. 3), since both of them presuppose that the fluid extends to infinity in all directions. Corrections for the effect of walls not too close to the sphere have, however, been worked out by Ladenburg, assuming Stokes's system, and by Faxén, assuming Oseen's system of differential equations. It has been pointed out by Faxén[9] that Oseen's objections to the simplification adopted by Stokes disappear if the fluid is not infinite in all directions but is bounded by a wall not too remote, i.e. if not only R^2 but also $\frac{\zeta}{d} \cdot R^2$ are small, where ζ is the distance of the wall from the centre of the sphere. The wall corrections given are not identical, however, even when $\frac{\zeta}{d} \cdot R^2$ is small, although they should agree when this term becomes negligible and higher powers of ζ/d than the first are disregarded. These corrections will be discussed in § 5 (a); here we proceed to deal with experimental investigations into the validity of Stokes's and Oseen's Laws. As may be gathered from some of the references which are given later, there is little doubt of the accuracy of Stokes's Law at very low velocities: the object of our analysis is to find the upper limit for the validity of each of these laws.

Since in most applications of Stokes's resistance formula it is

the terminal velocity of spheres falling under the influence of gravity which is considered, it is frequently convenient (Allen[10]) to introduce the conception of a critical radius $\bar{a}$, such that when a sphere of this radius falls by its own weight in a fluid of density ρ, the velocity attained will be that required to make $v\bar{a}\rho/\eta$ equal to unity as in Rayleigh's criterion. If v in this expression be replaced by the value calculated from Stokes's Law, we have

$$\frac{2}{9}\frac{\bar{a}^2(\sigma-\rho)g}{\eta}\cdot\frac{\bar{a}\rho}{\eta}=1,$$

or

$$\bar{a}=\left\{\frac{9}{2}\frac{\eta^2}{g\rho(\sigma-\rho)}\right\}^{\frac{1}{3}}\quad . \quad . \quad . \quad . \quad \text{(VIII. 4)}$$

The character of the motion may then be expressed numerically either by the actual value of va/ν, or by the ratio of the radius of the sphere used to the critical radius. Either number will of course be non-dimensional, and from the definition of the critical radius it is obvious that $va/\nu = a^3/\bar{a}^3$. In what follows we use $R = \dfrac{vd\rho}{\eta}$ where d is the diameter of the sphere, in order to avoid confusion of nomenclature, hence $a/\bar{a} = (R/2)^{1/3}$.

∕Allen[10] made measurements on air-bubbles rising in aniline and in water, on paraffin wax spheres rising in aniline, and on amber and steel spheres falling in water. His experiments covered a wide range of values of R (0·008 to 8,000), but many in the neighbourhood of $R = 1$ were lacking in accuracy owing to the use of air bubbles (see § 7). A more detailed investigation of the limits of validity of Stokes's Law was made by Arnold,[11] who observed the rates of fall of spheres of Rose metal in colza oil and in linseed oil, and of spheres of beeswax in transformer oil and in aqueous alcohol. His results led him to conclude that inertia terms begin to have an appreciable effect on the calculated viscosity when $a/\bar{a} = 0·6$; the mean from the four series is actually $a/\bar{a} = 0·67$. Since his curves appear to be accurate to about 0·5 per cent., although the individual observations of which they express the mean show much greater variations, the sum of the terms involving v^2 is indicated as less than 0·5 per cent. of the sum of those expressing the viscous resistance when the radius is two-thirds of the critical radius.

The data of Allen and of Arnold, together with some results obtained by Silvey[12] for the fall of mercury droplets through castor

oil, at much lower values of R, and with some figures taken from the preliminary paper by Liebster and Schiller[13] of which more anon, have been collated by Castelman.[14] Plotting the ratio of resistance per unit area of cross-section to ρv^2 against R, in logarithmic co-ordinates so as to embrace a wide field, he finds that the experimental points fall on a continuous curve. Up to $R = 0\cdot5$, or $a/\bar{a} = 0\cdot6$ roughly, the curve is indistinguishable from, i.e. is within 1 or 2 per cent. of, the straight line required by Stokes's Law, and at $R = 1$ the divergence is less than 7 per cent.; thereafter the ratio falls less rapidly but does not approach constancy until $a/\bar{a}$ is of the order of 14, when the resistance becomes practically independent of the viscosity and proportional to ρv^2. He considers that the more extended agreement with the formula of Stokes which is indicated by some of Arnold's results is due to the fact that eddies could not form freely behind the sphere in that worker's narrowest fall tube, i.e. that the correction applied for the effect of the walls was too high in the case of the larger spheres.

The curves of Castelman, of Liebster, and of Lunnon,[15] which are of the form shown in Fig. 34, agree in the absence of any indication of a discontinuity such as that found for the flow of fluids in pipes (Fig. 4), corresponding with the passage from a stream line or laminar to a turbulent condition. Although it has been stated (Nisi and Porter)[16] that eddies are first formed when the relative motion of the sphere and the fluid is defined by a value $R = 8\cdot15$, other experiments (Williams)[17] have failed to demonstrate the production of such turbulence even at $R = 720$. It is probably inadmissible, however, to apply conclusions obtained from the flow of fluids past a stationary sphere to the apparently analogous case of the translation of a sphere, since the motion relative to the walls is different in the two cases.

A photographic method devised by Hirsch[18] allows records to be obtained of the distances traversed by a falling sphere in successive short measured intervals of time. This method was employed both by Liebster[19] and by Schmiedel.[20] The experiments of the former investigator covered a very large range of Reynolds's numbers, $R = 0\cdot135$ to 2,000, and the results give an excellent picture (cf. Fig. 34) of the variations of resistance with the different régimes of fluid flow. Schmiedel's data are confined to much lower values of R ($R < 1\cdot5$ in most cases) and he appears to have been able, consequently, to secure a higher degree of accuracy in the

range in which we are here interested. Steel balls were used by both workers, Schmiedel including also two aluminium spheres to obtain lower velocities. Though the velocity was varied by adjusting the concentration of solutions of glycerol, the main factor on which Schmiedel relied to vary the value of R from one experiment to another was a change in the diameter of the sphere which was to be photographed. This makes it rather difficult to analyse the
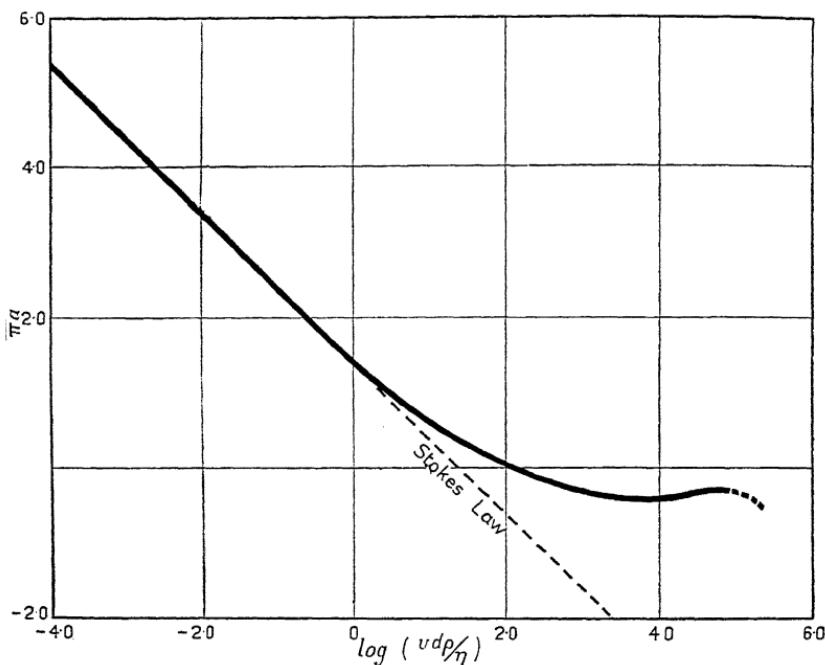

Fig. 34. Resistance to the motion of a sphere.

results, since the effect of a gradual variation in the wall-correction tends to be superimposed on that of the variation of R. Schmiedel anticipated this criticism to some extent, however, by making a second series of experiments in which the wall-correction was increased by halving the diameter of the cylinder in which the spheres fell. Liebster's solutions differed more widely in viscosity, and the ratio (diameter of sphere)/(diameter of tank), usually fairly low, did not increase at all regularly with R; unfortunately the errors were too high to give a precise indication of the nature of the failure of Stokes's or Oseen's Laws in the neighbourhood of $R = 1$.

Both of these authors present their results in the form of curves

in which the 'resistance ecefficient' $\psi = W \div (\pi a^2 \cdot \frac{1}{2}\rho v^2)$ was plotted against R, using logarithmic scales as in Fig. 34. Expressed in these dimensionless terms, Stokes's Law appears as $\psi = 24/R$ and is therefore represented by a straight line making an angle of $45°$ with the axes, while Oseen's Law is represented by a curve: most of the experimental points lay between the two graphs when the appropriate wall-correction had been applied. For our purposes the data may more conveniently be rearranged to show the relative error which would arise if the velocities and diameters were used to calculate the viscosity. I have therefore plotted in Fig. 35 the ratio η^1/η against R, where η is the viscosity as determined by the capillary-tube method and η^1 that calculated from the falling-sphere experiments. As in the original papers, the calculation of η^1 has been made by two different methods,

(a) assuming Stokes's Law to be true, in which case the Ladenburg correction* is used to eliminate the effect of the walls;

(b) assuming Oseen's Law to hold and correcting for the walls by means of Faxén's equation.

If either law held accurately up to $R = 1.5$, the points calculated by that law should of course lie on the horizontal straight line $\eta^1/\eta = 1.00$. The fact that Schmiedel's results tend towards a fairly constant value greater than unity at the lower Reynolds's numbers may probably be ascribed to errors in his capillary-tube determinations, for which he claims no greater accuracy than ± 1 per cent.; the fact that he used the Hagenbach correction for kinetic energy, instead of the more accurate Boussinesq correction (see Chap. II, § 4) would tend to make his values for η low, i.e. to make η^1/η greater than 1.00. The slope rather than the position of the mean curve should therefore be made the criterion: I have preferred not to attempt to draw the mean curve but to connect Schmiedel's points by a series of straight lines, leaving the mean to be inferred. Liebster's results are shown by other points which are not similarly connected.

The two series of results due to Schmiedel, in the first of which d/D (diameter of cylinder $= D$) varied between 0.018 and 0.036, while in the second the variation was from 0.037 to 0.074, enable us to judge the extent to which the form of the curve is influenced by inaccuracy in the method of correction for the presence of the

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* With the coefficient 2.4; but the results of this and of earlier investigations should be recalculated with the coefficient 2.1 (see foot-note p. 181).

wall. So long as the wall correction does not introduce error, the mean curves given by the two series should be indistinguishable. On this criterion the Faxén correction appears to be justified up to $R = 0.5$; at higher values of R the value of η^1 deduced by its application is too low, i.e. the correction to the velocity is definitely too large. The Ladenburg correction begins to produce an error of the same nature at $R = 0.2$.

If the resistance to motion has been calculated by a law which takes no account, or insufficient account, of the contribution due to inertia effects, the resistance actually experienced will naturally be higher than that calculated. Hence the apparent viscosity η^1, deduced from the experimental data by the application of Stokes's Law, would be expected to be higher than the true viscosity, especially at the greater values of R. This expectation is confirmed by the upper curves of Fig. 35, and if allowance be made for the fact that the wall correction is too high above $R = 0.2$, it will be seen that the deviation from Stokes's Law above this point becomes even more pronounced than appears from the tests in the larger cylinder. Oseen's Law tends to make too large a correction for inertia effects, at any rate above $R = 0.8$.

We may conclude from Schmiedel's results, with which Liebster's are not inconsistent, that Oseen's Law holds up to $R = 0.8$ with an error not exceeding about 1 per cent.; and that the Faxén correction holds with an error less than 1 per cent. up to $R = 0.5$, at any rate so long as the container has a diameter more than 15 times that of the sphere. The failure of the correction at this point is not surprising, since it is calculated on the assumption that R^2 is negligible (Faxén).[21] The same assumption is made in the derivation of Oseen's Law itself.

At $R = 0.2$, the value of the correction in Oseen's equation is nearly 4 per cent. The upper curves of Fig. 35 would appear to indicate, however, that Stokes's Law holds up to this speed with an error not greater than 1 per cent.: the contradiction may be explained by supposing that the Ladenburg correction (which is about 8 per cent. in both series near this point) is too large. This supposition also explains the fact that η^1/η remains in the neighbourhood of unity when calculated from the tests in the narrow tube up to $R = 0.75$.

A similar explanation is offered by Faxén[21] to show that Arnold's experiments, which appear to show extended agreement with

Stokes's Law, are not actually, as Weyssenhoff suggests,[22] in disagreement with the requirements of Oseen's Law. As mentioned above, Castelman is also prepared to discredit Arnold's results for
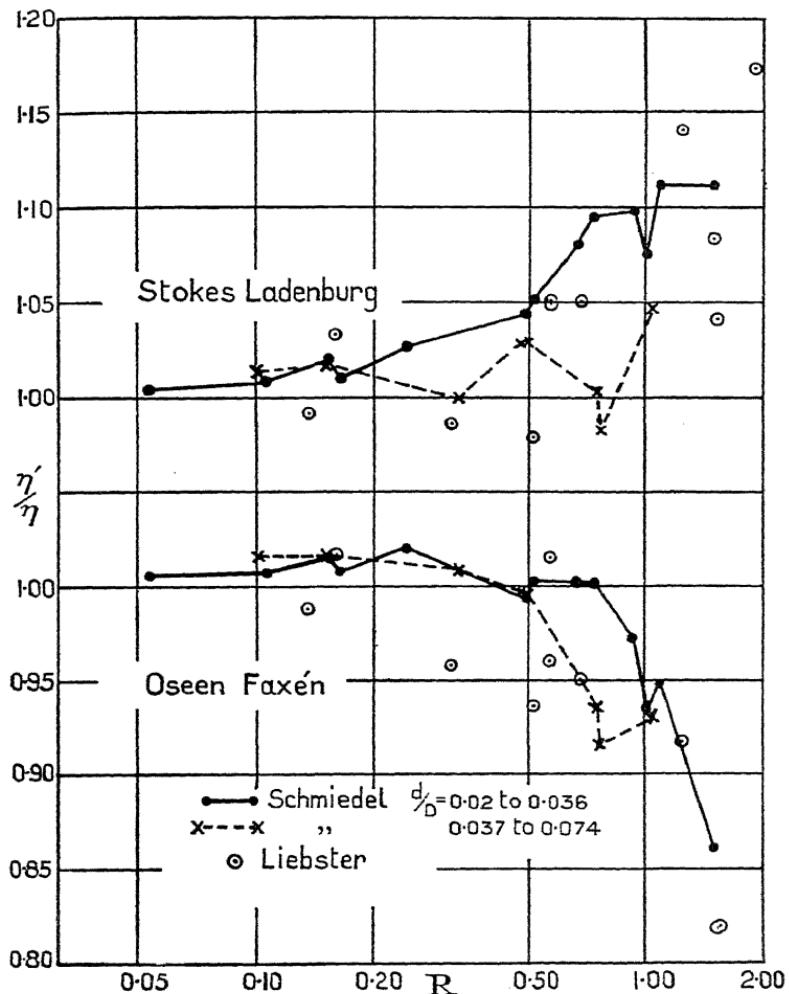

FIG. 35. Limits of applicability of Stokes's and Oseen's Laws.

the same reason. The older data of Allen, which were made under conditions such that the wall correction should be insignificant, are definitely in better accord with Oseen's than with Stokes's Law. Many other investigations have been cited as offering experimental proof of the truth of Stokes's Law, but these have been at low values of R; if the accuracy is not better than 1 per cent. it is

obviously impossible to discriminate between the two formulae at rates of fall corresponding with Reynolds's numbers lower than about 0·05.

4. Examination of the assumptions involved. It is assumed, in the derivation both of Stokes's and of Oseen's equations, that

(1) the motion of the sphere relative to the fluid is slow,

(2) the fluid is of infinite extent,

(3) the fluid is homogeneous,

(4) the sphere is rigid,

(5) the motion is steady and free from accelerations, and

(6) there is no slip between the fluid and the sphere.

With the first of these assumptions we have already dealt: we may expect to obtain measurements of viscosity accurate to about 1 per cent., if we decide to apply Stokes's Law, only when the conditions are such as to make R less than 0·05, or with Oseen's Law only when $R < 0·8$. Assumption (6) may be paraphrased as stating that the fluid in immediate contact with the sphere moves with the same velocity and in the same direction as the sphere: it has already been discussed in connexion with the development of Poiseuille's Law (Chap. II, § 8): here it will be made tacitly except in so far as it requires modification in the discussion of (3). The other assumptions, and the corrections arising from their inapplicability in certain cases, are the subjects of the following sections.

5 (a). The correction for the effect of the walls. In calculating the results of his experiments on the fall of fairly large spheres in a tall tank of square section, Newton[23] recognized the necessity of applying a correction for the influence of the walls of the vessel. Assuming that the resistance to the movement was proportional to the square of the velocity, he indicated that, to eliminate the effect of the walls, the distance traversed should be multiplied by $\dfrac{A}{A-\pi a^2} \cdot \left(\dfrac{A}{A-\frac{1}{2}\pi a^2}\right)^{\frac{1}{4}}$, where A is the cross-section of the tank; his proof is somewhat involved. For the fall of lead shot in water Munroe[24] suggested the approximate formula $v/v_\infty = 1 - (d/D)^{3/2}$, where v is the velocity observed, v_∞ that calculated for an infinite medium, and d and D are the diameters of the sphere and of the containing cylinder respectively. Lunnon[25] finds experimentally

the formula $v/v_\infty = 1 - 0\cdot23\,d/D$ for the régime of rapid movement $(R > 1000)$. The first serious attempt to deduce a correction mathematically for the laminar régime was a calculation by Lorentz[26] for the effect of one infinite plane wall on the resistance:

he found $W = 3\pi d\eta v\left(1 + \dfrac{9}{32}\cdot\dfrac{d}{\zeta}\right)$ where ζ is the distance from the

centre of the sphere to the wall. Stock[27] carried Lorentz's calculation a stage further and found

$$W = 3\pi d\eta v\left[\left(1 - \frac{9}{32}\frac{d}{\zeta}\right)^{-1} - \left(\frac{d}{4\zeta}\right)^3\right]. \quad . \quad \text{(VIII. 5)}$$

A more complete formula, based on Oseen's equations, is given by Faxén.[28] In the above formulae it is assumed that the sphere moves parallel to the plane wall and that the fluid is of infinite extent in all other directions. These conditions are not simulated in any practical method of viscometry.

For the important case of a sphere moving along the axis of a cylinder Ladenburg[29] applied Lorentz's method of calculation and found that for an infinitely long cylinder of diameter D the resistance corresponds with a velocity of the sphere relative to the fluid of

$$v\,(1+2\cdot4\,d/D), \quad . \quad . \quad . \quad \text{(VIII. 6)*}$$

when v is the observed velocity relative to the walls. The correction is a first approximation only, and Weyssenhoff remarked[30] that a closer approximation is very desirable, especially as it appears to be 'a mere matter of arithmetic'; the further calculations, which are lengthy and laborious even when all inertia terms are neglected, have been made by Faxén (vide infra).

If the coefficient of d/D be deduced from Ladenburg's own experimental results by plotting the uncorrected viscosity against d/D and drawing the 'best straight line' through the twelve points, a value $2\cdot6$ is obtained. But the points for each sphere in the different tubes actually lie on a curve convex to the d/D axis,

* Dr. H. Faxén (private communication), after expressing extreme admiration for Ladenburg's contributions to science, points out that there is a slip in the evaluation of the coefficient in this formula and that Ladenburg's own summation equation leads, when the computation is correctly carried out, to a value $2\cdot1$, as in (VIII. 8), in place of the $2\cdot4$ of (VIII. 6). I have quoted the Ladenburg correction in the familiar form which has been used in many experimental investigations, but the coefficient $2\cdot4$ has obviously no theoretical basis in view of the above criticism.

indicating that the correction is not strictly linear. This led me to suggest[31] that the correction factor to be assumed from an examination of his data is, more approximately $(1 + 2 \cdot 4 \, d/D + 2 \cdot 4 \, d^2/D^2)$. Arnold[32] found that the usual Ladenburg factor was too small when d/D was greater than $0 \cdot 1$: similarly, Gibson and Jacobs[33] showed that there was an error of about 2 per cent. at $d/D = 0 \cdot 14$ and of 9 per cent. at $d/D = 0 \cdot 19$. The suggested emendation would go far towards removing these divergences, but the above purely empirical formula is inconsistent with Faxén's analysis, which shows the absence of any term involving $(d/D)^2$.

The fact that Ladenburg's correction becomes subject to an uncertainty of one or two per cent., when the fall tube has a diameter only ten times that of the sphere, necessitates the use of somewhat inconveniently large tubes when liquids of high viscosity are under investigation. The quantity of material required for a test is increased, the sighting of the sphere is rendered more difficult, especially if the liquid is highly coloured, and the temperature control becomes more and more troublesome as the fall-tube is made wider. Sheppard[34] attempted to find an empirical correction which should be applicable to higher values of d/D; for this purpose he measured the rates of fall of steel balls having diameters of $\frac{1}{4}$, $\frac{3}{8}$, and $\frac{1}{2}$ inch in tubes of various bores containing a nitrocellulose solution the viscosity of which he estimated as about 390 poises. Since a correction having the linear form given by Ladenburg will obviously cease to apply when $d/D = 1$, he proposed to correct the time of fall to that in an infinite medium by subtracting $cd^2/(D - d)^2$, where c is a constant for any size of ball and is roughly proportional to the reciprocal of the weight of the ball. Although the formula leads to values of the viscosity which usually vary not more than ± 3 per cent., when calculated from data obtained with one sphere, up to $d/D = 0 \cdot 3$, the conceptions leading to it appear unsound. Further, the liquid used was one which is now known to be liable to have its apparent viscosity affected by the rate of shear (see Chap. XI); the corrected times for the $\frac{1}{2}$ inch spheres lead, in fact, to viscosities 8 per cent. lower than those obtained by means of the $\frac{1}{4}$ inch spheres, a divergence which Sheppard ascribed to the effect of the ends of the fall-tube, but which is in the direction to be expected for a medium having a variable apparent viscosity.

The failure of Ladenburg's correction when d/D is increased

above about 0·1 is well shown by some recent measurements made by Lunnon,[35] who dropped steel balls through glycerin in a cylinder of 2·25 cm. diameter and found that the balls had a maximum velocity when their diameter was 0·8 cm., i.e. at d/D about 0·35.

We have already seen, however, in § 3, that Stokes's system of equations, which forms the basis of Ladenburg's calculations, is inadequate except for very low values of $vd\rho/\eta$. When the motion is not extremely 'slow' it is desirable, therefore, to take into account the semi-quadratic terms discarded by Stokes and to examine the result obtained by including them in the deduction of the wall correction. For the effect of the wall on the motion of a sphere along the axis of an infinite cylinder containing a viscous fluid Faxén,[36] starting from Oseen's system of equations, arrives at a formula which may be written

$$W = 3\pi d\eta v \div \left\{ 1 - \frac{3}{16}R - \frac{d}{D}f\left(\frac{D}{d}\cdot R\right) + 2\cdot09\left(\frac{d}{D}\right)^3 - 0\cdot95\left(\frac{d}{D}\right)^5 \right\}.$$

$$\text{(VIII. 7)}$$

He gives values of a function analogous to $f\ (D/d\ .\ R)$ for a few values of the argument: these are reproduced in the following table together with three others which I have interpolated between $D/d\ .\ R = 0$ and $D/d\ .\ R = 2$.

$\dfrac{D}{d}\cdot\dfrac{vd\rho}{\eta} = 0$	0·2	0·4	0·8	2·0	4·0	8·0	20·0
$f\left(\dfrac{D}{d}\cdot R\right) = 2\cdot104$	2·07	2·03	1·96	1·76	1·48	1·04	0·46

The formula is derived on the assumption that $(vd\rho/\eta)^2$, $R\,(d/D)^2$, and $(d/D)^6$ are negligible compared with unity. When R^2D/d is also negligible, the formula simplifies to

$$W = 3\pi d\eta v \div \left\{ 1 - 2\cdot104\frac{d}{D} + 2\cdot09\left(\frac{d}{D}\right)^3 - 0\cdot95\left(\frac{d}{D}\right)^5 \right\}, \quad \text{(VIII. 8)}$$

which can be derived more readily from Stokes's system of equations and forms a closer approximation than Ladenburg's when the velocity is so low that it is permissible to use Stokes's Law.

The assumptions involved in formulae (VIII. 7) and (VIII. 8) should not be overlooked when these expressions are used in estimating the viscosity from experimental data. Thus, if an accuracy of 0·1 per cent. is contemplated at $R = 0\cdot03$, d/D must obviously be less than 0·18. For the experimental proof that the

correction equation (VIII. 7) holds up to $R = 0\cdot5$, within about 1 per cent., see the discussion of Schmiedel's experiments (§ 3).

5 (b). Effect of the ends of the tube. The cylinder used in practice is obviously not of infinite length, as assumed in Ladenburg's or Faxén's analysis, so Ladenburg[37] proceeded to calculate the effect of the two ends. For the case of a sphere moving at right angles to one infinite plane, Lorentz[38] had previously shown that the resistance was increased over that in an infinite medium by the factor $\left(1 + \dfrac{9}{16}\dfrac{d}{l}\right)$ where l is the distance of the centre from the plane. Ladenburg calculated that a sphere falling between two infinite rigid horizontal planes distant h from one another experiences a resistance proportional to $v\,(1 + 1\cdot65\,d/h)$ instead of to v if the fall is timed over the middle 5/12 of the distance h: if timed over the middle 4/5 of h, the average relative velocity becomes $v\,(1 + 2\cdot25\,d/h)$. It may be remarked, in this connexion, that the factor $(1 + 1\cdot65\,d/h)$ has frequently been misapplied to cases where the initial and final distances of the sphere from the ends are other than $7/24 \,.\, h$.

Considerable objection may be taken to the application of the second of Ladenburg's corrections, viz. that for the effect of the ends of a cylinder on the rate of fall of a sphere. In the first place, the calculations assume that the ends are infinite planes, whereas they usually subtend a very small solid angle at the centre of the sphere, and the presence of the cylindrical walls will naturally modify the 'reflected flow' postulated in Lorentz's method. Secondly, as pointed out by Weyssenhoff,[39] the terms of which the correction gives the sum are alternately positive and negative and the series converges so slowly that the summation requires to be carried much further than Ladenburg has taken it; even when this has been done the result would need to be treated as the first term of another series which would require summation to yield an accuracy similar to that obtained for the effect of a wall parallel to the direction of motion.

Fairly strong evidence may be adduced also from the experimental side pointing to the conclusion that under most conditions the correction for the ends is negligible. Several observers remark incidentally that the rate of fall of the sphere was found to be constant when measured over successive sections of the tube in

which it was moving, although the end-correction would obviously not be constant for all positions. Ladenburg[37] found some justification for the proposed amplification of Stokes's formula in the fact that the viscosity of his Venetian turpentine, calculated by its means, approximated to the value (1325 poises) deduced from experiments by the Poiseuille method, more closely than if the correction was omitted. But the viscosity was shown to vary by 25 per cent. per 1° C., a coefficient which makes extremely severe demands on the reproducibility of the temperatures prevailing in different arrangements of apparatus. Actually, the application of the correction makes the mean of the twelve recorded determinations become subject to a probable error of 1·5 per cent., while without it the probable error appears as 1·0 per cent.

Sheppard[40] deduced from his own experiments with a nitro-cellulose solution a correction factor $(1 + 5·8d/h)$ which, he admitted, 'appears rather large'. As shown above, the medium was almost certainly one of which the apparent viscosity varied with the rate of shear, and the correction found empirically was merely an attempt to make the apparent viscosity independent of the size of the sphere. His results lead, in fact, to a correction which is the reciprocal of that which he enunciated; he seems to have overlooked the sign of the discrepancy.

In the recent investigation to which we have already referred in § 3, Schmiedel made a special series of experiments to decide on the end correction which should be applied to his results. The conditions of his experiments differed from those postulated in Ladenburg's analysis in that the liquid was bounded at the top, not by a solid wall, but by a free surface in contact with air. When the velocity of a ball of 0·19 cm. diameter was measured over the middle third of the column of liquid in a tank of 8·5 cm. square section, he could detect no difference between the results obtained for liquid columns of 9 cm. and 18 cm. If Ladenburg's correction were applicable to these conditions, there should have been a difference of about 1·6 per cent. Replacement of a free surface by a solid cover was also without measurable effect when d/h had the value 0·01. He was able, however, to obtain an approximate verification of Lorentz's formula (*vide supra*) by measuring the velocity over very short intervals as a ball of 1 mm. diameter approached the bottom of the tank. He therefore proceeded to apply a correction based on this formula to his experiments in

cylindrical tubes; the actual correction was obtained, as in Laden-burg's method, by finding the mean velocity over the middle third of the fall by integration, and was evaluated as $1\cdot2\dfrac{d}{h}\,.\,v$. The difference between this and the Ladenburg value $1\cdot65\dfrac{d}{h}\,.\,v$ was within the error of the measurements.

It is possible, however, to find in Schmiedel's record fairly strong evidence indicating that the correction should really be made much smaller if the vessel is of relatively small diameter. Thus, in each series, the velocity began to decrease rapidly only when the distance from the bottom was reduced to about six times the diameter of the ball; the corrected velocities in this neighbour-hood tended to be appreciably higher than those at a distance of 60 or 70 diameters. Since the diameter of the equivalent tank of circular section was 96 times that of the sphere, it seems as though the end correction tends to vanish when the distance of the ball from the end is comparable with the distance from the side walls: similarly, the wall correction presumably tends to vanish when the ball approaches closely to a solid end. It would appear to be preferable, therefore, to apply no end correction to measurements made as in Schmiedel's cylinders, where the ends were always at least 4 times as remote as were the side walls from the falling sphere.

5 (c). Sphere between infinite parallel walls. Before leaving the subject of the corrections to Stokes's Law necessitated by the finite extent of the fluid in which the sphere moves, mention may be made of the case in which the fluid is bounded by two infinite planes. Boundary conditions of this type are fulfilled, to a suffi-cient degree of approximation, in certain measurements made with the object of determining the size of colloidal particles from their rate of sedimentation in a liquid of known viscosity, and the con-verse problem may possibly have some importance. For a sphere moving parallel to and midway between infinite planes, when the speed is so low that Stokes's Law may be supposed to apply rigidly, Faxén[41] calculated the resistance as

$$W = 3\pi d\eta v \div \left\{1 - 1\cdot004\frac{d}{l} + 0\cdot418\left(\frac{d}{l}\right)^3 - 0\cdot169\left(\frac{d}{l}\right)^5\right\}, \quad \text{(VIII. 9)}$$

where l is the distance apart of the planes: he found that the

formula agreed with the experimental results of Westgren[42] at least as well as that author's empirical equation, already criticized by Weyssenhoff, in which the resistance for an infinite medium is multiplied by $\left(1 + 3 \cdot 4 \dfrac{d^2}{l^2}\right)$. Faxén has also calculated[43] the value of the resistance for a case in which the centre of the sphere is three times as far from one wall as from the other; the coefficient of d/l becomes 1·305 and the sphere rotates as though it were rolling down the more remote wall. For a sphere in Brownian movement[44] the expression becomes somewhat complicated.

5 (d). Mutual effect of two spheres. The influence of the presence of other falling solid particles on the fall of a sphere in a viscous medium is of considerable importance in the theory of sedimentation, but need not much concern us here. It will suffice to refer to the simplest of such modifications, viz. that in which two spheres traverse the same path, one being a distance l, measured between centres, in advance of the other: this is a case which may occur in practical viscometry if duplicate determinations are being made. If the spheres have equal diameters and weights, they fall at the same speed, the resistance to the motion of either of them being given by the following equation (Faxén[45]; cf. also Smoluchowski,[46] Oseen,[47] and Stimson and Jeffery[48]):

$$W = 3\pi d\eta v\left(1 - \frac{3}{4}\frac{d}{l} + \frac{9}{16}\frac{d^2}{l^2} + \dots \text{higher powers of } d/l\right). \quad \text{(VIII. 10)}$$

It is assumed that the Reynolds's number is so small that it may be neglected in comparison with unity. An error of 0·5 per cent. would thus arise in a measurement of viscosity by the falling sphere method if a second ball were released when the first had travelled 150 diameters.

6. Effect of inhomogeneity of the fluid. In the derivation of Stokes's Law and in Oseen's and Faxén's treatment, it is assumed that the distances between the particles of the fluid are negligible compared with the diameter of the sphere. For true liquids this assumption appears to be always justified in practical viscometry and to result in the absence of any slip at the solid-liquid surface: thus Arnold[49] showed that the coefficient of sliding friction (which would be infinity if there were no slip and zero for infinite slip) was at least 5,000 for colza oil and at least 50,000 for castor oil in

contact with Rose metal. In the case of gases, it is obvious that on the kinetic theory the mean free path of the molecules may, at low pressures, become comparable with or greater than the diameter of the sphere. Cunningham[50] calculated that the resistance offered to the motion should be reduced below that given by Stokes in the ratio $1:(1 + A\lambda/a)$ where λ is the mean free path of the molecules, a the radius of the sphere and A a constant for which he indicated a value between 0·857 and 1·71. Zerner[51] pointed out a defect in the calculation, on remedying which the value of the constant became 1·575. More recent recalculations are due to Lenard[52] and to Epstein.[53]

In his earliest experiments Millikan[54] deduced $A = 0·817$ on the assumption of the existence of the electron, which was indicated by his work. Ehrenhaft used a value $A = 0·815$, confirmed by optical measurements.[55] Subsequently Millikan found that a more complicated correction was in better agreement with experiments designed for its evaluation. The form used is one suggested by Knudsen and Weber[56] to reproduce the results which they obtained for the logarithmic decrement of the oscillations of a platinum rod carrying a glass sphere at each end and suspended by its mid-point in a gas, viz.

$$W = 6\,\pi\eta\,av \div \left\{1 + \frac{\lambda}{a}(A + Be^{-ca/\lambda})\right\} . . \quad \text{(VIII. 10 a)}$$

A full theoretical discussion of the formula and details of the experimental evaluation of the constants are given in an important paper by Millikan.[57]

A similar formula was adopted by Mattauch,[58] whose paper contains a critique of previous determinations. The values of the three constants are given by different authorities as:

	A	B	c
Knudsen and Weber	0·773	0·400	1·63
Millikan	0·864	0·290	1·25
Mattauch	0·898	0·312	2·37

Millikan's and Mattauch's values refer to oil-drops in air and in nitrogen respectively; the American worker gives reasons for assuming that the constants are independent of the material of the sphere.

The correction above discussed is of fundamental importance in general physics, but since its use in practical viscometry is necessarily limited, this brief *exposé* must suffice here.

7. Fluid spheres. The movement of liquid drops and gas bubbles in a viscous liquid. The difficulty of obtaining very small solid spheres of accurate figure has tended to restrict the use of the falling-sphere method to the viscometry of liquids having viscosities not less than about ten poises. Steel ball-bearings, for example, cannot regularly be obtained with a diameter less than 3/64 inch, and such balls fall in an oil of the above mentioned viscosity at a rate of some 0·5 cm. per sec., so that for accurate observation of the velocity by timing the fall through a measured distance, the oil column required is already inconveniently long. If smaller spheres were available a reduction could be made not only in the length of the tube but also in its diameter, which has to be many times that of the sphere in order to avoid too large a wall correction. It has occurred to several investigators that sufficiently accurate spheres might be obtained by forming bubbles of a gas or drops of a chemically indifferent and immiscible liquid in the fluid to be examined. Thus Jones[59] used droplets of mercury in measuring the viscosity of glycerine: he adopted an ingenious method, of which the principle is given below, for accurately determining the masses of the droplets (of the order of 3 to 10 milligrammes) by means of an ordinary chemical balance.

Let a mass M of some 0·1 gm. of mercury be weighed out and subdivided into about 12 approximately equal drops of unknown masses $m_1, m_2 \ldots m_{12}$. Next let the velocities of fall $v_1, v_2, \ldots v_{12}$ of each drop in a sample of glycerin or of oil be observed at one temperature. Since the viscosity is proportional to a^2/v, where a is the radius, i.e. to $m^{2.3}/v$, we have for a constant viscosity $m = kv^{3/2}$, whence $M = \Sigma m = k\Sigma(v^{3.2}) = kV^{3.2}$, where V is the velocity with which the whole mass M would have fallen through the liquid if Stokes's Law still held as accurately for it as for the smaller drops. Hence

$$\eta = \frac{2}{9}\left(\frac{3\,M}{4\,\pi\sigma}\right)^{2/3} g\,\frac{\sigma-\rho}{V} \qquad \text{and also} \quad \frac{m}{M} = \left(\frac{v}{V}\right)^{3.2}.$$

In this manner m may be determined (to 0·1 per cent. readily) and each droplet so standardized becomes available for other measurements of viscosity.

A practical hint in connexion with the formation of gas bubbles for viscometric purposes is given by Allen,[60] who states that bubbles formed at the end of thick-walled capillaries have practically constant sizes, but the diameters of those blown from fine

thin-walled tubes vary with the pressure and with the rate of formation.

The assumption that Stokes's Law applies to fluid spheres was examined by Rybczynski,[61] and independently by Hadamard.[62] The correction formulated by them is usually known by the name of the French worker. A derivation is given by Lamb,[63] and, with the use of another method, by Bond.[64] The resistance to the motion of the sphere is shown to be

$$W = 3\pi d\eta v k, \qquad k = \frac{2\,\eta + 3\,\eta^1}{3\,\eta + 3\,\eta^1} \qquad \text{(VIII. 11)}$$

where η^1 is the viscosity of the fluid of which the drop is composed. The correction term obviously reduces to unity for $\eta^1 = \infty$ and to $2/3$ for $\eta^1 = 0$. Experiments with different pairs of fluids should therefore give rates of rise or fall of the sphere varying from 100 to 150 per cent. of those predicted by Stokes's Law. Measurements were made by Roux[65] and later by Silvey[66] on mercury drops in castor oil: Roux used drops of 1·2 to 1·8 mm. diameter and worked at a temperature of 14° C., corresponding with $\eta^1/\eta = {}^1/1320$, while in Silvey's experiments the drops varied from $d = 0\cdot12$ to $d = 0\cdot76$ mm. and the temperature was 25° C., for which $\eta^1/\eta = {}^1/425$. Nordlund[67] made observations on mercury droplets of 0·02 mm. diameter in diluted glycerol. But in no case did the predicted increase in velocity occur: the rate of fall agreed closely with that required by Stokes's Law except that Roux found deviations, in the direction expected, of 6 per cent. for his smaller and 10 per cent. for his larger drops.

The existence of a circulation of the fluid inside the drops, which is required by the Hadamard theory, becomes obvious when large drops such as those of alcohol in olive oil or of aniline in water contain accidental solid impurities or minute bubbles; a similar but more restricted circulation may be inferred for smaller drops of these liquids.

It is assumed in the derivation of the above correction that there is no tangential force, i.e. that there is no discontinuity of velocities, at the surface of the sphere. Boussinesq[68] applied the conception of a superficial viscosity to the mathematical treatment and was led to modify the correcting term of equation (VIII. 11) to

$$k = \frac{\epsilon + a\,(2\,\eta + 3\,\eta^1)}{\epsilon + a + (3\,\eta 3\,\eta^1)}, \qquad \text{(VIII. 12)}$$

where ϵ is the coefficient of surface viscosity (actually the sum of two coefficients, one for each side of the surface). The formula leads to values of resistance intermediate between those required by Stokes's Law with and without the Hadamard correction, and shows that all fluid spheres of very small radius should move like solids; it is also in qualitative agreement with Roux's result, that larger drops tend to show divergences from Stokes's Law, the divergences increasing with the radius. Weyssenhoff[69] draws attention to the fact that Arnold's data for air bubbles in olive oil show all stages from agreement with Stokes's Law, for bubbles of less than 0·2 mm. diameter, to agreement with the Hadamard formula, for bubbles of diameter 0·8 to 1·0 mm. But in the absence of any extraneous data for the values of the coefficient of superficial viscosity it is impossible to obtain a quantitative test of the theory from the above experiments.

The problem has recently been studied by Bond[64] and by Bond and Newton[70] both practically and theoretically. In Bond's first experiments he observed the rate of rise of air bubbles in waterglass and in golden syrup ($\eta = 400$ to $2,000$ poises) and found $k = 0·7$. For drops of water and of golden syrup in castor oil the experimental values of k were 0·86 and 0·94 respectively; the Hadamard formula would require $k = 0·67$ and $k = 1·00$ in these last two cases and $k = 0·67$ in the air-bubble tests. The distribution of velocities in the liquid in the neighbourhood of the bubbles was examined by a photographic method and found to be in accordance with the equations of motion obtained by an extension of Stokes's theory when the appropriate values of k were introduced into the formulae.

Consideration of the divergences of k from the Hadamard equation led Bond and Newton to investigate the effects of surface forces involved in the transference of an element of the common surface from the axis of motion of the sphere, where the tangential velocities are both nearly zero, to the equatorial plane, where the velocities are a maximum; the transference connotes an increase in the area of the element and, hence, an expenditure of work which will modify the original equations. Treating the problem by the method of dimensions, they suggest that in the neighbourhood of a critical radius a^1, given by

$$a^1 = \left\{ \frac{T}{|(\sigma - \rho)|g} \right\}^{1\,2} \qquad . \qquad . \qquad \text{(VIII. 13)}$$

where T is the interfacial tension, the value of k should show a transition from that corresponding with a solid sphere, $k = 1$, to that corresponding with the Hadamard formula (VIII. 11) which may fall to 0·67 if η^1/η is small.

Curves representing the results of experiments made to check this theory show that for small diameters of drops or bubbles the value of k approaches unity very closely, and that when the diameter is sufficiently increased k becomes equal to 2/3. The transition between the two values also occurs at a radius not far from that expected, as shown by the following table in which a^1 *exp.* is the radius, found on the curves, at which $k = 0.8$.

	η^1/η	T	$\rho - \sigma$	a^1	a^1 *exp.*
Air in water glass	10^{-7}	104	-1.69	2·5 mm.	1·0 mm
Air in golden syrup	10^{-6}	91	-1.48	2·5 ,,	1·1 ,,
Mercury in syrup	10^{-4}	285	12·1	1·5 ,,	1·2 ,,
Water in castor oil	10^{-3}	18	0·037	7·0 ,,	7·7 ,,

It may be noted that Bond modified the form of the Ladenburg corrections (VIII. 6 and § 5b) for the effect of the wall in his experiments by multiplying by k the ratios d/D and d/h which occur therein; this necessitated a method of successive approximation in the deduction of k from the observations. The wall correction was determined experimentally for solid spheres and the substantial accuracy of the form adopted was confirmed by making some of the measurements in containers of different diameter.

The interfacial tension at surfaces such as that between water and castor oil is not constant, and in some cases the interface tends to become more or less rigid after some time. The latter phenomenon appears to explain why Arnold[71] found that air-bubbles in linseed oil behaved almost as if they were solid. Arnold also observed a curious erosion of bubbles of air in a number of liquids. The erosion was found to be such that the area of cross-section diminished uniformly with the distance travelled, even though the bubble had remained practically unchanged for several hours while it was at rest. The mechanism is possibly analogous to that which is seen when a large drop of alcohol traverses some olive oil, the surface layer being torn off, leaving a cloud of minute droplets behind; in the case of air-bubbles the only change visible is the decrease in size.

8. Uniformity of the motion. The solution obtained by Stokes for the terminal velocity of a sphere falling in a viscous medium is a limiting case of his more general solution for the oscillation of a pendulum. The complete expression for the resistance offered to the slow motion of a sphere acted upon by gravity is not only difficult to obtain but is of complicated form (Picciati[72], Boggio[73]). As it is desirable to have some idea of the distance or time of fall which must elapse before the terminal velocity may be considered to have been attained, within the experimental error, an approximate method of calculation may be indicated. Neglecting those terms the complete expression which define the effect of the previous motion of the sphere upon the condition of the fluid, the velocity of the sphere at any time t after its release is given by Weyssenhoff[69] as

$$v = \frac{2}{9} a^2 g \frac{\sigma - \rho}{\eta} (1 - e^{-pt}), \qquad \text{(VIII. 14)}$$

where
$$p = \frac{9}{2} \frac{\eta}{a^2 (\sigma + \frac{1}{2}\rho)}.$$

The velocity is thus within ϵk of the constant terminal velocity k

$\left(= \frac{2}{9} a^2 g \frac{\sigma - \rho}{\eta} \right)$ when $e^{-pt} = \epsilon$ i.e. $t = -\frac{1}{p} \log \epsilon$.

The total distance s travelled in this time is given by integration of (VIII. 14) between the limits 0 and t;

$$s = \frac{k}{p} (-\log \epsilon - 1 + \epsilon).$$

If Stokes's Law is to be applied, the radius a of the sphere must be less than the critical radius $\bar{a}$ (VIII. 4), so that

$$\frac{k}{p} < \frac{2}{9} \bar{a} \frac{\sigma + \frac{1}{2}\rho}{\rho},$$

as may be seen by putting $a < \bar{a}$ after substituting for k and p. Hence
$$s < \frac{2}{9} \bar{a} \frac{\sigma + \frac{1}{2}\rho}{\rho} (-\log \epsilon - 1 + \epsilon). \quad . \quad \text{(VIII. 15)}$$

Now for steel balls falling in oil, &c., $\dfrac{\sigma + \frac{1}{2}\rho}{\rho}$ is about 9, so that in such cases we have

for $\epsilon = 0\cdot1$ $s < 1\cdot4$ diameters,
$\epsilon = 0\cdot01$ $s < 3\cdot6$,,   ,
$\epsilon = 0\cdot001$ $s < 5\cdot9$,,   .

The spheres used in practice will normally, of course, have a

radius considerably smaller than the critical; for a given deviation from the terminal velocity the number of diameters traversed varies as the volume of the sphere, consequently it is only in exceptional cases that appreciable error should arise from the delay in reaching the constant speed which is assumed to prevail.

An illuminating contrast between the régimes of laminar and turbulent flow of the fluid around a moving solid is afforded by a comparison of the maximum distance, 3·6 diameters, calculated above for $\epsilon = 0·01$ at a Reynolds's number of unity, with the figure deduced by Lunnon[74] for the case of rapid fall. Lunnon estimates that a steel sphere of diameter 1·83 cm. travels 26,000 diameters in air before it attains 99 per cent. of its constant terminal velocity.

Most experimenters have arranged to make their observations of terminal velocity, for purposes of viscometry, after the sphere has fallen considerably more than six diameters. For this procedure there are two reasons. One is the difficulty of releasing the ball from rest without disturbance such as would lead to deviation from an axial path through the container. The other is the effect of the presence of any releasing apparatus on the initial rate of fall; of the extent of this effect some idea may be obtained from Lorentz's formula (§ 5 b) for the influence of an infinite plane wall perpendicular to the direction of motion or from the formula (VI. 4) cited in connexion with the Michell viscometer. A further practical advantage is that when the sphere has travelled slowly through a considerable column of liquid some opportunity has been afforded for the attainment of thermal equilibrium, for the removal of surface films of impurities from the sphere, &c.

Liebster[75] cites a number of observations showing that the velocity over consecutive small intervals of the total path varied from the mean by more than the probable error. The deviations did not seem to exhibit any periodicity such as would be expected from a theory involving the production of eddies behind the sphere. Since slight variations in the direction of travel also occurred, it is perhaps reasonable to ascribe both types of disturbance to the presence of microscopic solid particles in suspension or to the existence of convection in the liquid. Similar variations in velocity are reported by Schmiedel.[76] Several observers have noticed that a sphere which begins to fall axially down a vertical tube is occa-

sionally nearer to one side or other towards the bottom and that such deflections are not necessarily accompanied by any definite increase in the time of fall.

9. Fall of bodies other than spheres. The effect of deviations from the spherical shape was analysed some fifty years ago by Oberbeck by assuming that the falling body was an ellipsoid of revolution; the calculation may be found in Lamb's *Hydro-dynamics*. It appears from the general formulae for slow motion (obtained as in Stokes's system of equations) that when a body, having three planes of symmetry at right angles to one another, falls through an infinite fluid it experiences no turning moment, i.e. there is no preferred orientation. This is contrary to trivial observation, since leaves, &c., falling in air or flat bodies falling in water are known to tend to avoid travelling edgewise, but such motion cannot be described as slow in the sense of § 3 above. The deduction may, however, be readily verified by allowing sufficiently small and light disks to fall in a viscous liquid. Schmiedel[76] mentions that it was confirmed in his experiments in the region of laminar flow (apparently up to $R = 1$); at higher values of the Reynolds criterion the horizontal position became the more stable, while above $R = ca.$ 80 his disks invariably oscillated.

Oberbeck's formulae have been applied by Gans[77] to the calculation of correction terms to Stokes's Law for oblate and prolate spheroids. If the three semi-axes of an ellipsoid of revolution be a, b, and c, where $a > c$, and the resistance be expressed as

$$W = 6\pi\eta\, av/\delta \quad . \quad . \quad . \quad \text{(VIII. 16)}$$

then, if $(c/a)^2$ may be neglected in comparison with unity, Gans finds the following values for δ:

Disk moving edgewise $\delta = \dfrac{9}{16}\pi\left(1 - \dfrac{8}{3\pi}\cdot\dfrac{c}{a}\right)$. (VIII. 16 a)

,,   ,,   broadside on $\delta = \dfrac{3}{8}\pi$ . . . . . (VIII. 16 b)

Rod moving lengthwise $\delta = \dfrac{3}{4}\left(2\log\dfrac{2a}{c} - 1\right)$ (VIII. 16 c)

,,   ,,   broadside on $\delta = \dfrac{3}{8}\left(2\log\dfrac{2a}{c} + 1\right)$ . . (VIII. 16 d)

If, on the other hand, $(1 - c/a)$ is so small that its square may be neglected in comparison with unity, we have

Oblate spheroid $(a = b)$ moving

in equatorial plane $\qquad \delta = 1 + \dfrac{2}{z}\Big(1 \qquad c \qquad\qquad$. (VIII. 16 e)

along polar axis $\qquad \delta = 1 + \dfrac{1}{5}\Big(1 - \dfrac{c}{a}\Big) \quad$ . . (VIII. 16 f)

Prolate spheroid $(b = c)$ moving

in equatorial plane $\qquad \delta = 1 + \dfrac{3}{5}\Big(1 - \dfrac{c}{a}\Big) \quad$ . . (VIII. 16 g)

along polar axis $\qquad \delta = 1 + \dfrac{4}{5}\Big(1 - \dfrac{c}{a} \qquad$. (VIII. 16 h)

Values of δ are tabulated in Gans's paper for ratios c/a varying from 0 to 1. He points out that if none of the axes of symmetry be vertical the ellipsoid will not fall vertically: the extremes of deviation are shown by a disk inclined at 50° 19′ to the vertical, which should fall in a direction making 11° 32′ with the vertical, and by a rod inclined at 35° 16′ to the vertical, which should fall in a direction making 19° 28′ with the vertical.

The last four formulae above enable us to obtain an estimate of the error which will be introduced into a determination of viscosity by the falling-sphere method by slight lack of sphericity. It appears that if there is a difference of 1 per cent. between the maximum and minimum diameters, these being at right angles to one another, the error may vary from 0·2 to 0·8 per cent. according to the orientation which the ball assumes, if the diameter used in the calculation is the maximum. Actually, however, one would prefer a mean value, obtained from three measurements at right angles or else deduced from the weight of the ball: calculation shows that in this case a maximum error of 1 per cent. in viscosity might arise from a difference of 8 per cent. in the diameters. These remarks apply, of course, only to regular shapes: minute imperfections, rust spots, &c., may produce other errors due, for example, to the trapping of air-bubbles.

The formulae given by Gans for the resistance offered to the motion of disks and rods suggest two modifications of the falling sphere method which may be of use occasionally, at any rate for approximate viscometry. The lower limit of viscometry for which the method can be applied is determined, as far as routine work is concerned, not by the failure of Stokes's Law owing to the Reynolds's number approaching unity, but by the fact that steel

ball-bearings, which are almost the only spheres of good figure readily obtainable, cannot generally be bought in sizes smaller than 3/64 inch diameter and the velocity of such balls soon becomes too high to be observed by timing with a stop-watch over a distance of 15 to 20 cm. Now a disk having a diameter of, for example, 40 times its thickness, travels, even when falling edge-wise, only about three-fifths as fast as a sphere of the same weight and material, as may be seen by comparison of the formulae. Since many materials other than steel may be obtained in the form of thin sheet from which fairly accurate disks may be punched, it is possible to reduce the velocity of the falling body considerably without having recourse to microscopic spheres. A disk with the above-mentioned ratio of diameter to thickness has only about three times the diameter of a sphere of equal weight: hence the size of the containing vessel need not be prohibitive, assuming that the correction for the proximity of walls is approximately the same as for a sphere of equal diameter. The edgewise position, though giving a velocity about $1\frac{1}{2}$ times as great as the broadside-on, is the more easily reproducible by simple releasing apparatus and is less liable to be disturbed during fall by the fact that the centre of gravity may be slightly displaced from the centre of the disk.

Towards the other extreme of the range of viscosities which may be encountered in practice, a limit is reached beyond which it becomes inexpedient to increase the velocity of the sphere in a very viscous medium by increasing the size of the steel ball. Here a rod falling axially might replace the sphere: thus instead of using a $\frac{1}{4}$-inch ball in a tube of $2\frac{1}{2}$ inch bore, we might use a rod of the same weight, e.g. a little over 1 inch of 1/10 inch diameter rod, which would fall at about the same rate in tubing of one inch bore. Further, as in the case of disks, the material need not be steel; a heavy metal like tungsten would give the advantage of increased speed of fall.

The formulae of Oberbeck and of Gans are based on the assumption that all inertia terms may be neglected. Taking into account the 'semi-quadratic' terms, Oseen[78] suggested that a correction should be necessary somewhat similar to that which he had deduced for the case of a sphere. For a disk falling broadside on, his equation is

$$W = 16\eta a v \left(1 + \frac{R}{2\pi}\right). \quad . \quad . \quad \text{(VIII. 17)}$$

. This differs from the expression given above (VIII. 16 b) only by

the addition of the term in brackets. Schmiedel[76] finds that this formula is in good agreement with the data he obtained for the fall of steel disks in glycerol solutions up to a Reynolds's number of 1·07, if allowance be made for the effect of the walls by assuming that Faxén's correction is applicable to this case as well as to that of a sphere. If, however, it had been assumed that Ladenburg's correction is applicable, the results would have accorded almost equally well with the Oberbeck formula. No theoretical investigation appears to have been made of the effect of the walls in modifying the conditions of fall of a body of any shape other than spherical.

10. Experimental details.

(a) *Selection of sphere.* (i) Material. It will be assumed in what follows that steel balls are to be used, since if any other material be selected it will generally be necessary to construct the spheres for the purpose. It is extremely difficult to turn spheres of 1 to 2 mm. diameter on the lathe with the requisite accuracy. The only other method which has been used at all extensively is to rely on surface tension to produce the desired form in liquid drops. There may, however, be objections to the direct application of Stokes's Law to the fall of liquid drops or to the rise of gas bubbles (see § 7 above), at any rate unless they are very small. Hence some workers have used solidified droplets, e.g. of Rose metal, of wax or of sulphur, produced by forcing the molten material from a small orifice through a column of a suitable cooling fluid long enough to allow the liquid to congeal. The spheres formed are frequently pitted (cf. Arnold[79]), but, if they are small and have solidified while falling slowly, they are of good general figure. The most suitable materials for use in this method are such as may be cooled many degrees below their freezing point before crystallization begins; substances, such as glass and selenium, which will remain amorphous at room temperatures are naturally to be preferred, *caeteris paribus*. Small[80] recommends the use of $\frac{1}{8}$ inch glass spheres in the viscometry of cellulose solutions, but I have no data regarding their commercial production.

Unless some accurate method of grading be employed, however, all the spheres produced by such methods require to be carefully measured, in at least three directions, before or after use. The hardened steel balls supplied for ball-bearings are subjected to such a grading as part of the process of manufacture. The makers

usually guarantee the spheres not to differ by more than one ten-thousandth of an inch from the nominal diameter, when measured in any direction; as a consequence of the method of adjustment, in which a very large number of balls are ground at once between two plates, the balls of any one batch do not usually differ by more than one or two hundred-thousandths of an inch from one another. For many purposes it is therefore sufficiently accurate to assume the diameter to be that stated, and when higher precision is required only a few balls of a batch will normally need to be measured. Occasionally a ball may be found to fall consistently slower than others alleged to be similar; such discordance is usually traceable to the presence of small pits on the surface. A spot of rust is liable to produce the same effect; balls should therefore be stored under oil or with a coating of vaseline, the adhering film being removed, e.g. with benzol, before use.

Schmiedel[76] mentions a point which may be of use to other investigators who measure the diameter of polished spheres under the microscope. He found a difficulty in setting the cross-wire of the eye-piece to touch the image of the circumference of the ball, owing to the brilliance of reflection of the light, but the adjustment was much facilitated by placing two similar balls in contact and in line with that being measured.

(ii) Dimensions. The size of the sphere most suitable for use will depend upon the order of magnitude of the viscosity which is to be determined and upon the means to be adopted for timing the fall. Photographic and electrical chronographic apparatus will allow short intervals of time to be recorded with accuracy, and such devices are necessary in certain circumstances, but for routine work a good stop-watch is much more convenient. If a stop-watch reading to $\frac{1}{5}$ second is to be used, the time of fall must obviously be not less than 40 secs. if an accuracy of $\frac{1}{2}$ per cent. is demanded. Assuming that the ball may be timed over a length of 40 cm., the maximum velocity which can be postulated is then 1 cm. per second. Application of Stokes's Law leads to the following estimates for the minimum viscosities which can be measured, on the foregoing assumptions, by means of steel balls of various diameters:

Diameter of ball, inches	3/64	1/16	3/32	1/8	3/16	1/4	3/8	1/2
Viscosity, poises	6	10	25	40	100	170	380	680

(Balls of 3/64 inch diameter are not always readily obtainable,

though it is sometimes possible to procure balls as small as 1 mm.)
These estimates will of course be reduced if a lower accuracy is
sufficient; an accuracy of $\frac{1}{2}$ per cent. is not likely to be attained at
the higher viscosities. It may be remarked that in all the cases
tabulated the motion is extremely 'slow' in the sense of § 3; the
value of $a/\bar{a}$ for a 1/16 inch ball falling in an oil having a viscosity
of 10 poises is only 0·077: for a $\frac{1}{2}$ inch ball in a liquid of 680 poises,
$a/\bar{a} = 0·037$. In the next section it will be shown that it is desirable
to use smaller balls than are suggested by the above table, i.e. to
work at speeds slower than 1 cm. per sec.

(b) *The fall-tube.* The most suitable dimensions of the fall-tube in
which the motion of a selected sphere is to be observed will again
depend on the accuracy which is desired. As has been mentioned
in § 5 (a), several observers have noticed that the Ladenburg
correction for the effect of the walls becomes inadequate when the
diameter of the vessel is reduced to ten times the diameter of the
sphere. Faxén's correction, confirmed by Schmiedel to about
1 per cent. for $D/d = 15$, is numerically almost indistinguishable
from that of Ladenburg at the low Reynolds's numbers with which
we are now concerned. There appears to be no certainty of avoid-
ing an error of $\frac{1}{2}$ per cent. unless the tube has a diameter at least
20 times that of the sphere.

The necessity of making the wall correction small is best met
by selecting a sphere smaller than is given in the table in the
preceding section. Thus, if the viscosity is about 40 poises, a
1/16 inch ball is preferable to a $\frac{1}{8}$ inch ball in that the diameter
of the fall-tube may be reduced from 3 inches to $1\frac{1}{2}$ inches; this
reduces the volume of liquid required for a test and makes it much
easier to maintain constancy of temperature and to avoid the
probability of convection currents. The use of the smaller ball
tends also to avoid errors in timing or to decrease the necessary
length of the path over which the observation is made: additional
economy of liquid and facilitation of temperature control are
afforded by exploitation of the latter alternative.

With the object of reproducing the conditions specified by
Ladenburg in the calculation and experimental verification of his
correction for the ends of the cylinder, it has been usual to suggest
that the fall of the sphere should be timed over the middle 5/12
of the length of the tube: few investigators have gone so far,

however, as to provide a rigid top. Since it is frequently desirable to make the time rather longer, there has been a tendency to utilize a larger proportion of the column of liquid, and the middle half has been adopted, e.g. by the British Engineering Standards Association.[81] Arguments have been advanced in § 5 (b) to show that the correction should not be applied at all so long as the termination of the path over which the fall is timed is not nearer to the ends than one or two times the diameter of the tube. These views may not be generally accepted, but it will be admitted by the majority that it is desirable to select a tube so long that the Ladenburg correction is not more than 1 per cent., whether the correction is or is not applied. On this criterion, the height of the column of liquid to be used with a sphere of 1/16 inch diameter is roughly 10 inches, the fall being timed over some 4 inches at the middle. Similarly, for the same ball, a column of 14 inches might be used and the movement timed over the middle 11·2 inches corresponding with the factor 2·25 calculated by Ladenburg for such conditions. When the viscosity is so high that a 1/16 inch ball gives an inconveniently slow rate of travel, and a larger ball becomes requisite, adherence to the same ratios of height of liquid column to diameter of sphere would necessitate the use of tubes so long as to make the thermostatic arrangements troublesome; fortunately, errors of considerably more than $\frac{1}{2}$ per cent. are usually to be tolerated on high viscosities.

Workers who have been accustomed to time the fall of a sphere over the middle third of the tube may have some fears as to whether the constant terminal velocity will be attained if the first fiducial mark is only 1·4 inches from the top of the column of liquid, as would be the case in the second example suggested in the last paragraph. If the ball is at the same temperature as the liquid, the considerations advanced in § 8 show, however, that the terminal velocity is established almost as soon as the ball is released when the motion is as slow as it is in the conditions here postulated.

The fall-tube is usually provided with etched marks which define the beginning and end of the distance over which the fall is to be timed. In most cases it is convenient to observe the motion directly; the marks must then be continued round from the front to the back of the tube in a plane at right angles to the axis so that the eye may be placed in this plane when waiting for the ball to reach the mark. When the ball is very small or the

motion so slow that a short path only is to be traversed, it becomes convenient to avoid parallax error and to obtain a little magnification by the use of a reading telescope of low power, such that the ball and a mark on the front of the fall-tube are in focus at the same time. For the use of X-ray skiagrams in observing the motion of a sphere in an opaque liquid or inside a furnace see Masson, Gilbert, and Buckley.[82]

Other marks are frequently placed on the tube dividing the length normally used for timing into two, or preferably three, equal parts so that the uniformity of the velocity may be checked. Such additional etched rings may be of value when the homogeneity of the liquid is not above suspicion. Since the liquid does not completely fill the tube, space being provided for the insertion of a cork and a releasing device, another mark may be added to indicate the level to which the tube is to be filled. In some work carried out by Miss Hadfield and me[83] in which the contents of the fall-tube were somewhat sensitive to light, the tube was surrounded by an opaque screen in which there were slits of 3–4 mm. at the levels of the fiducial marks. When the time of fall was expected to exceed a few minutes it became convenient to have a preliminary estimate of the total time required; this was obtained by providing an additional mark a short distance above the first fiducial mark, and noting the time required to traverse this short distance. It was then possible to switch off the light, for the greater part of the time of fall, returning to look through the lower slit for the appearance of the ball only when it was nearly due.

(c) *The thermostat.* Since the falling-sphere method is normally used only for liquids of high viscosity, which invariably have high temperature-coefficients of viscosity, it is necessary to arrange for accurate regulation of the temperature. In such liquids, moreover, equalization of small differences of temperature depends almost entirely on conduction of heat and is much slower than in less viscous liquids in which convection currents may be readily produced. The temperature of the bath must therefore be maintained uniform and constant for a long time before the actual beginning of a determination: the time required depends on the accuracy desired and on the diameter of the fall-tube, and may vary from half an hour to a day, so that automatic control is essential even for work of moderate precision.

In view of the length of the fall-tube it is usually necessary to set up a special thermostat to accommodate it, the baths supplied for other physico-chemical work being much too shallow. Provision must be made for rapid circulation of the bath liquid from top to bottom. Jones[84] showed that, if there were small variations of temperature along the path of fall, the time required for the sphere to traverse a given distance should be the same as that required when the column of liquid had a uniform temperature equal to the mean temperature of the non-uniform column. When, however, the bath is inadequately stirred, the distribution of temperature in the fall-tube differs from that in the bath liquid, and the mean assumed may be in error. The stirring mechanism should not introduce appreciable vibration.

Provision should be made for adjusting the fall-tube to the vertical. If the tube fits into circular holes in supports fixed near the top and bottom of the thermostat, the adjustment may be permanent.

The front wall of the thermostat is preferably of plate glass. If a cylindrical glass vessel be employed the appearance of the fall-tube and its contents is liable to be distorted and some error in the observation of the beginning and end of the fall is probable, particularly when a reading telescope is used and the fiducial marks are not rings extending from the front to the back of the fall-tube. Error due to such distortion may be corrected by observing through the telescope a steel measure placed along the axis of the tube filled with liquid.

(d) *Release of the sphere.* When thermal equilibrium has been attained, the cleaned sphere, previously brought to the same temperature as the liquid, is introduced axially into the fall-tube. Various devices have been employed for ensuring axial delivery with the minimum disturbance to the liquid. The simplest of these, which is extremely satisfactory, was described by Gibson and Jacobs[85] and consists of a glass tube 7 cm. long, having a bore slightly larger than the diameter of the ball. This tube passes through the middle of a cork fitting into the fall-tube and dips 3 cm. below the surface of the liquid under test. A small hole is blown through the wall, at a level above that to which the liquid will rise owing to its surface tension; this allows air to escape when the cork is being pushed in. Through such a tube the ball falls at a rate which is extremely slow compared with its subsequent

rate of travel; the interval of time occupied by the ball in passing through the release tube allows any small temperature difference between the ball and the liquid to become obliterated and gives adherent air-bubbles an opportunity of becoming detached. The depth of immersion and the diameter of the release tube have been modified by other workers according as a longer or shorter delay appeared desirable. The cork may be replaced by a glass tube fitting fairly closely into the top of the fall-tube and carrying the release tube sealed to it; this modification was suggested by Forster[86] and is illustrated in Fig. 36: I have added a slight flare at the top.

Air vent

Filling mark on Fall-tube
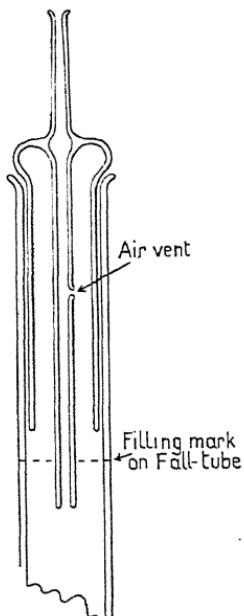
FIG. 36. Glass releasing device for falling-sphere viscometer.

Other devices for this purpose have been described. Ladenburg,[87] for example, used a curved tube extending from near the edge of the cover to the axis of the cylinder; Schmiedel[88] applied an electromagnet, the protruding pole-piece of which was enclosed in a glass sheath to avoid adherence, due to remanent magnetism, when the current was switched off. Extreme precision in centring is superfluous, since it is usually found that in spite of all precautions the path of the sphere does not remain truly axial. Slight deviations are not necessarily accompanied by a noticeable increase in the time of fall, at any rate when the tube has a diameter more than some 15 times that of the sphere.

(e) *Determination of densities.* The densities both of the fluid and of the material of the sphere occur in the formula from which the viscosity has to be evaluated. The determination of the former calls for little comment, since the accuracy required is low, at any rate when steel balls are to be used, an error of 0·01 on a density as high as 2 gm. per ml. producing in this case an error of 0·2 per cent. in the calculated viscosity. It is only when the density of the sphere is low, as when glass or aluminium balls, gas-bubbles or drops of a light liquid are employed with a view to reducing the velocity of fall, that any greater precision becomes necessary.

The densities of hardened steel balls appear to vary considerably from one batch to another, and smaller balls tend to be of lower density, possibly owing to being hardened to a relatively greater depth; thus I found 7·54 gm. per ml. for certain 3/64″ balls and 7·63 gm./ml. for 5/64″ balls. The densities may be obtained, when the weights have been determined, either by calculating the volumes from the measured diameters or with the aid of a pyknometer. Since a 3/64″ ball weighs rather less than 7 mgm., most workers have contented themselves with finding an average by weighing 50 or more together; even with such a number it is advisable, when the displacement method is used, to construct a pyknometer having dimensions more suitable than those of the specific gravity bottles normally available.

Ladenburg[87] preferred to minimize the effect of errors in the assumed density of his steel spheres by weighing each of them and modifying the usual form of Stokes's Law (VIII. 2) to

$$\eta = \frac{Gg\,(\sigma-\rho)}{3\,\pi\,dv\,\sigma}, \quad . \quad . \quad . \quad \text{(VIII. 18)}$$

where G is the mass of the sphere and the other symbols have their previous significance. If the weight can be determined with the required accuracy—a micro-balance is needed for the smallest balls—this method has two advantages:

(1) the density need not be determined exactly; thus, if ρ is in the neighbourhood of unity, an error of 0·1 gm./ml. in σ will produce an error of only 0·2 per cent. in η.

(2) the effect of an error in the assumed diameter is halved, since the first power, instead of the square, of the diameter appears in the formula.

For a method suggested by Jones for determining the masses of small droplets of mercury, of which the density may be assumed, see § 7 above.

11. Modifications of the method.

(a) *Relative measurements.* When the falling-sphere apparatus is required to furnish not an absolute determination of viscosity but a comparison between the viscosities of two fluids, certain limitations, such as those imposed by the inadequacy of the wall-correction, become of decreased importance. It is then possible to effect a number of simplifications in the procedure and, in

particular, to make the whole apparatus smaller and more convenient, so that temperature control is facilitated. It has been shown § 5 (a) that the ratio d/D cannot be increased above 0·05 if an accuracy of $\frac{1}{2}$ per cent. is desired in an absolute determination. But, whatever the exact form of the wall-correction may be, it is clear that for low velocities of the sphere (low Reynolds's number) the correction is practically independent of the viscosity. Hence there is no theoretical objection to reducing the relative diameter of the fall-tube as far as may be practically convenient. As the ratio d/D is raised, it becomes increasingly important, however, to preserve the same conditions in duplicate experiments so that even a fairly rigid specification is insufficient to make the fall-tubes interchangeable. It is best, if possible, to use the same sphere, as well as the same fall-tube, in making comparison between the viscosities of two liquids. Under these conditions the ratio of the viscosities is given by the formula

$$\frac{\eta_1}{\eta_2} = \frac{\sigma - \rho_1}{\sigma - \rho_2} \cdot \frac{t_1}{t_2}, \quad . \quad . \quad . \quad \text{(VIII. 19)}$$

where η_1 is the viscosity and ρ_1 the density of a liquid in which the ball falls from one fiducial mark to the other in a time t_1, while η_2, ρ_2, and t_2 refer to the liquid with which comparison is being made. In most routine work in which this method is used the densities of the liquids under test vary so little that a mean value may be assumed for ρ_1.

An example of the application of this method, in which the ratio d/D is increased to 0·18, is afforded by a tentative specification put forward by the Viscosity Committee of the Cellulose Division of the American Chemical Society.[89] In the proposed arrangement a $\frac{1}{4}$ inch steel ball is timed from a mark 5 cm. from the top to one 2·5 cm. from the bottom of a fall-tube 33 cm. long and of 3·5 cm. diameter. In a modification suggested by Small[90] for use with cuprammonium solutions of cellulose, a glass sphere of 3·3 mm. diameter is allowed to fall through a tube of 1·5 cm. diameter.

The correction for the effect of the ends of the tube disappears as well as that for the effect of the walls when the falling-sphere method is used to provide relative determinations only. Hence it is feasible, in comparative work, to extend the length of the path over which the fall is timed so as to reach very close to the ends; it is desirable to reserve a distance equal to at least two or three

times the diameter of the ball at each end so as not to exaggerate
unduly the effect of impurities which may collect there. When
the liquids under examination are very dark in colour, or when for
any other reason, such as the presence of a furnace around the
fall-tube, the sphere cannot be observed directly, it is frequently
possible to record the end of the fall by causing the sphere to close
an electrical circuit: for this purpose the ball is caught on suitable
contacts at the bottom of the fall-tube (see, for example, Fischer[91]).
The presence of such contacts and of the releasing device does not
usually interfere with the accuracy of a relative measurement. It
may be shown (cf. the equations of § 8) that the error due to the
time which elapses before the sphere reaches its terminal velocity,
after starting from rest, is negligible in most arrangements if the
path timed is not too short and there is not too great a difference
between the viscosities of the liquids compared. An approximate
analysis indicates that, if steel balls are used, the observed times
of fall should be multiplied by $(1 - 0.06 \ R/n)$ where R is the
Reynolds's number and n the length of the fall expressed in terms
of the diameter of the sphere. Hence the ratio of the viscosities
corresponding with the times of fall t_1 and t_2 is

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \left\{ 1 - 0.06 \left(\frac{t_2}{t_1} - 1 \right) \frac{R_2}{n} \right\}, \quad . \quad . \quad \text{(VIII. 20)}$$

where R_2 refers to the standard liquid which gives the time t_2.

Relative viscosities determined by the application of formula
(VIII. 19) may, of course, be expressed in absolute units, so as to
be independent of the apparatus employed, if the viscosity of a
suitable calibrating liquid is known. The Bureau of Standards
and the Physikalisch-Technische Reichsanstalt issue samples of
castor oil of which the viscosity is stated, but if a standard liquid
of higher viscosity is required, in order to obtain a time of fall
approximating to that given by the liquids under investigation, it is
necessary to determine the viscosity of some suitable liquid such
as a syrup by the less convenient absolute method already outlined.

When the diameter of the fall-tube is only a small multiple of
that of the sphere there appears to be less probability of accidental
deviation of the line of fall from the vertical axis.

(b) *Sphere partially counterpoised.* It is obvious that if the force
tending to depress the sphere is reduced, the rate of fall can be

made as small as may be desired. Though other means suggest themselves as being possible in some cases, the only method which has been much used for this purpose is the direct one of suspending the sphere from a light pulley or balance and adding weights to a scale-pan attached to the other side of the pulley. Owing to the necessity of providing the sphere with some means of suspension, the application of this modification has been restricted to liquids of fairly high viscosity, for which a large sphere may be used. Further, since the presence of the suspending wire may be assumed to exert some influence on the nature of the fluid flow about the sphere, and since it is usually inconvenient to make the wall corrections small, the method is employed only for relative measurements, calibration being effected by means of a liquid of appropriate viscosity. Apparatus of the type considered has proved valuable in the examination of opaque materials and, in particular, in work at high temperatures. For the latter purpose it offers many advantages: thus, the pulley and indicating mechanism may be removed far from the hot body and measurements may be made on melts contained in a fairly small crucible.

The extent to which the sphere may be counterpoised is limited by the friction in the bearings of the pulley which support it. Pulley wheels can be made and mounted on jewel bearings so as to turn definitely with a load of 10 mgm. Considerable improvement in sensitivity is obtainable, however, by omitting the unwanted portions of the circumference of the pulley; thus, Stott, Irvine, and Turner[92] used a specially constructed balance, to the arms of which sectors were fitted having their centre in the axis of rotation; the centre of gravity being adjusted to lie on this axis, the balance turned to 1 mgm.

Arndt[93] gives details of the apparatus set up by him for work at high temperatures and of the method of procedure. Actually he used a hollow platinum cylinder with hemispherical ends (total length 12 or 22 mm., diameter 10 mm.) instead of a sphere, but the manipulation and calibration are not affected by this difference. The cylinder was supported by a 0·2 mm. platinum wire extending outside the furnace and this was carried by a silk thread passing over a 27 mm. wheel having jewelled bearings; to the other end of the thread was attached a scale-pan. The position of the cylinder was indicated by a light pointer fixed to the pulley and moving over a graduated scale. The liquid was contained in a

platinum crucible 50 mm. high and 30–45 mm. in diameter: it was necessary to fill this always to a standard depth. The position of the pointer was noted when the cylinder was just resting on the bottom of the crucible and the fall was timed between marks corresponding with positions of the end of the cylinder 19·6 mm. and 15 mm. from the bottom. It is important that these relative positions should be reproducible: e.g. Arndt found that if the path timed was 10 mm. lower the average velocity was 12 per cent. smaller.

Stott, Irvine, and Turner[92] used a 10 mm. ball of platinum-iridium suspended by a wire of the same material from a thread attached to the above-mentioned balance. They timed the fall from a point 70·6 mm. to one 50·3 mm. from the bottom of a pot 100 mm. high and 63 to 83 mm. in diameter, which was always filled to the brim. These authors remark that the velocity decreased linearly with the depth of immersion, until the sphere was very near the bottom of the pot.

The weight of the sphere (or cylinder) is partially counterpoised and the times of fall between the selected marks are observed when different loads are placed in the scale-pan. By plotting the reciprocals of the times against these loads, straight lines are obtained which cut the load axis at a point indicating the 'zero load' x, under which the sphere is exactly counterpoised (including the frictional force) at the lower fiducial mark. If the load W in the pan is thus found to be equal to $x - \dfrac{c}{t}$, the viscosity of the liquid is proportional to c. It is more convenient to find x by the above graphical method than by attempting to counterpoise the sphere exactly when it is immersed in a viscous liquid. The calibration constant is determined by repeating the experiments with liquids of known viscosity at convenient temperatures. The containing vessel, which will normally be different from that used at high temperatures, since it requires to be immersed in a thermostat, must be an exact copy of the crucible as regards the dimensions of the portion in which the liquid rests: the liquid must be adjusted to the same height, and the path of the sphere must correspond accurately with that over which it was previously timed. Arndt used castor oil ($\eta = 6$ to 52 poises) as calibrating liquid, and the English workers above mentioned used golden syrup at temperatures from $10°$ to $28°$ C. ($\eta = 100$ to $2,000$ poises).

The calibration factor appears to be liable to vary slightly with the viscosity.

It will be recognized as a peculiarity of this adaptation of the falling-sphere method that the density of the liquid does not appear in the formula for the calculation of absolute values of viscosity from the time of fall. If the slope of the load-velocity graph is determined from two observations only, as would normally be the case in making routine measurements, the viscosity may be evaluated by the simple formula,

$$\eta = \frac{W_2 - W_1}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} K,$$

where T_1, T_2 are the times corresponding with the counterpoising loads W_1, W_2 in the pan, and K is a constant found by noting the times of fall of the sphere in the standard liquid when counterpoised with two suitable loads.

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ROTATIONAL AND OSCILLATIONAL VISCOMETERS

THE definition of the coefficient of viscosity (Chap. I, § 4) implies the measurement of the tangential force exerted by the friction of a fluid on a moving plane. The conditions imagined in this definition are rather far removed from those under which viscosity is measured by the capillary-tube and falling-sphere methods. There are, however, certain types of apparatus in which the operation of viscous forces is more directly apparent.

The 'infinite parallel planes' of the definition being incapable of experimental realization, measurements of the retarding force due to viscosity may be made by the use of a plate of limited area constrained to move in its own plane between two larger parallel plates. Such a method has in fact been used in the study of plastic materials (Chap. X, § C 1), when the forces acting on the plate may be rendered fairly large, but it would be difficult to make the experimental arrangements suitable for the examination of normal fluids. The edge-effects occurring in the use of a plate are avoided by the substitution of a cylinder moving in the direction of its axis through the liquid so that disturbing effects are confined to the ends: apparatus of this type will be considered in Chap. X, § C 2. In the present chapter we shall deal with the uniform or periodic rotation in a viscous fluid of certain simple solids of revolution about their axis of symmetry.

The mathematical analysis leading to the evaluation of the couple due to viscous forces acting on a body of revolution is very much more simple when the rotation is assumed to be slow and uniform than when the system is supposed to oscillate about a mean position. On the other hand the experimental arrangements are much more simple in the latter case, since the production of a uniform gyration, absolutely free from disturbances and tremors due to errors of figure or of alignment, makes very stringent demands on the mechanical construction.

A practical difficulty which is common to both types of apparatus arises from the smallness of the couples resulting from the shearing of normal fluids at such rates as are compatible with the required precision of workmanship or with the theoretical assumptions of 'slow' movement. In a few instruments the couple pro-

duced by rotation is measured by means of weights and pulleys, in which case the friction of the pulley system is liable to cause error. Since in the majority of the viscometers described in this section the couple is balanced by the torsion of a wire, it will be convenient here to summarize the factors which have to be taken into account in torsion experiments.

Note on the torsion of wires. It is shown, e.g. in Searle's *Experimental Elasticity*,[1] that the couple G, required to twist through an angle ϕ the free end of a cylindrical wire of which the other end is fixed, is given by the relation

$$G = \tfrac{1}{2}\pi n a^4 \phi / l, \quad . \quad . \quad . \quad . \quad \text{(IX. 1)}$$

where l is the length, and a the radius of the wire and n the 'rigidity' of the material of which it is composed: the rigidity is defined as the tangential stress required to produce unit shear. The value of n for a given material depends considerably on the thermal and mechanical history of the sample: wires of steel and phosphor-bronze usually have rigidities of the order of $8 \cdot 5 \times 10^{11}$ and $4 \cdot 5 \times 10^{11}$ dynes per square centimetre respectively, but even with a given wire the rigidity may vary slightly with the weight of the suspended system.

If a suspended system is acted upon by so small a couple that the deflexion produced is too minute for accurate measurement, it is obvious from the above formula that reduction of the diameter of the suspension wire will rapidly increase the sensitivity. It is necessary, however, to avoid too near an approach to the elastic limit of the material of the wire; with a given load the tensional stress is proportional to $1/a^2$. Zemplén[2] sought to maintain the strength of the suspension by using two fine wires soldered together at their ends: a more common suggestion is to replace the wire by a strip, which gives a much greater deflexion for the same cross-section, but Harrington[3] found certain objections to this practice.   ⌣

Early workers employed wires having lengths up to 150 cm., but the tendency in later years has been towards shorter suspensions (15 to 25 cm.). It is difficult to obtain long straight wires, and any residual coil in a suspension leads to inconstancy of zero: Harrington found that the uncoiled stock from which steel 'hair springs' are made was very satisfactory. Very long wires are not easily maintained at a constant or uniform temperature and the rigidity

decreases with rise of temperature ($\frac{1}{4}$ per cent. per 1° C. for steel), except in a few special materials such as 'Elinvar'. The use of quartz fibres was suggested by Hogg:[4] this material offers the advantages of high tensile strength and low rigidity (3×10^{11} dynes per square centimetre); the temperature-coefficient of rigidity is very low, and is of the opposite sign to that of most metals.[5] Stout filaments of fused quartz have not the same properties as thin fibres, so that the use of this material is restricted to those cases where the suspended system weighs only a few grammes.

When subjected to exceedingly small torsional strains hard-drawn wires appear to be perfectly elastic, but as the twist per unit length is increased every wire eventually begins to assume a semi-permanent 'set', i.e. ceases to return at once to its original zero when the deflecting couple is removed. The critical value for the strain required to produce a set naturally depends on the accuracy of observation, but it is in general fairly sharply defined. The set decreases exponentially when the wire is allowed to rest without applied strain, and if not too severe it will usually become negligibly small after a day or two: oscillation eliminates the set much more rapidly. If deflexions require to be corrected for set, the larger readings in an interrupted series of observations should be taken last so as to diminish the uncertainty in applying the correction, obtained in preliminary determinations of the sets corresponding with different deflexions. Errors of this nature are minimized by working with a small maximum deflexion, the required precision of observation being obtained e.g. by the use of a mirror and scale.

For absolute determinations of viscosity by the rotation method the value of n may be found either by a static or dynamic experiment. The static method consists simply in applying a known couple to the given length of wire and observing the deflexion produced. Usually the couple is that due to a known force acting tangentially at the circumference of a pulley of known radius: in order that the wire may hang vertically, the force is preferably divided into two equal forces acting at opposite ends of a diameter. Weights, suspended by threads passing over a pair of pulleys, may be used with stout wires, but with the fine wires necessary for the viscometry of such fluids as water or air the friction of the pulleys would introduce too large an error. One method used for the measurement of very small forces is that in which a silk thread

carrying a weight W is deflected from the vertical by a horizontal pull and the deflexion θ is observed: the pull is then equal to $W \cos \theta$.

The dynamic method is more commonly employed. The sphere, disk or cylinder which is to be immersed in a rotating liquid, or else a specially constructed object of known moment of inertia, is suspended from the wire to form a torsional pendulum and the time of vibration is observed. It may be shown[6] that, if t is the time for one complete oscillation,

$$t = 2\pi \sqrt{\frac{2\,Il}{\pi na^4}} = \frac{2}{a^2} \sqrt{\frac{2\pi Il}{n}}, \quad . \quad . \quad . \quad \text{(IX. 2)}$$

where I is the moment of inertia of the suspended system: if M is the mass of the system, $I = 2/5 . MR^2$ for a solid sphere of radius R oscillating about a diameter, and $I = \frac{1}{2}M (a^2 + b^2)$ for a hollow cylinder having an external radius a and internal radius b, oscillating about the common axis. Since the cylinders used in rotation viscometers are frequently thin-walled, their moment of inertia is not always calculable with the required accuracy: further, there are necessarily some additional parts, such as the attachment for the wire and the pointer or mirror, of which the inertia requires to be taken into account. Hence the rigidity of the wire has usually been determined either (1) by substituting for the normal suspended system an inertia bar or accurately measured cylindrical annulus of approximately equal weight, or (2) by adding a body of known moment of inertia: from the times of vibration with and without this body in position two simultaneous equations are obtained from which I and n may be calculated. The latter method avoids the necessity for interfering with the attachment of the wire but involves an increase in the tension which may produce a change of rigidity: the change may be estimated by making a third observation of time with an added body of different weight.

The dynamic method tends to give higher values for the rigidity than are obtained by the static method: if the wire is one which assumes even a small permanent set under the strain applied, this set has to be reversed every time the pendulum passes through the zero position. The effect of the use of an unsuitable material or of excessive amplitude of vibration is, however, most marked when the wire forms the suspension of an oscillational viscometer.

Here, in order to eliminate errors due to the friction on certain parts not immersed in the liquid under examination, a 'blank' determination of logarithmic decrement is made when the main viscous forces are inoperative. Part of the decrement so found is due to the friction of air on the mirror, &c., but a proportion which may be considerable must be ascribed to the internal friction of the wire. This internal friction or 'elastic hysteresis', to which Thomson (1865) first drew attention, was studied in some detail by Tomlinson[7] and has been found to vary with time, with temperature and with the mechanical conditions. The hysteresis of a suitable wire may be brought to a reproducible value by causing it to oscillate a few hundred times through a certain arc under the given load.

The elastic defects of wires subjected to torsion have prompted many investigators to make use of bifilar suspensions, particularly in oscillational viscometers in which elastic hysteresis would be important. It is shown in the older text-books that if a bifilar suspension consisting of two flexible filaments of length l, at distances apart e_1 and e_2 at the extremities, be twisted from its zero position, the restoring couple G/ϕ per unit angular deflexion (cf. equation IX. 1) is given by

$$G/\phi = W \cdot e_1 e_2 / 4 l, \quad . \quad . \quad . \quad \text{(IX. 3)}$$

where W is the weight of the suspended system ($+$ half the weight of the filaments). If the rigidity of the filaments be not negligible, correction terms may be introduced into the above expression,[8] their magnitude being calculated from a determination of the rigidity. Since the distances e_1 and e_2 cannot usually be measured with the required precision, the value of the restoring couple to be introduced into the equation for the calculation of viscosity is determined by observing the time of oscillation t of a body of known weight W and moment of inertia I attached to the suspension: then

$$t = 4 \pi \sqrt{\frac{I l}{W e_1 e_2}} = 2 \pi \sqrt{\frac{I \phi}{G}} . \quad . \quad . \quad \text{(IX. 4)}$$

If the body used for this determination is not that which forms part of the viscometer, or if the apparent weight is varied by differences of buoyancy, the appropriate alteration of W must be made before applying the above expression to the viscosity equation.

The use of bifilar suspensions is subject, however, to certain limitations. In the first place, the rotation of the lower end entails a vertical displacement which is objectionable not only because it involves the action on the suspended system of forces not considered in the mathematical analysis, but also because it affects the clearance between the hanging body and the container. In the case of a suspended cylinder, for which the latter objection would be least important, variation of the minute clearance between it and the guard rings may cause trouble. Silk filaments have found favour in view of their strength and flexibility: but in many instruments the changes of their length which occur with time or with variations of humidity are prohibitive. Gilchrist[9] used a pair of narrow phosphor-bronze ribbons rolled from fine wire, but Harrington[10] found inconstant results with them in a similar apparatus, and preferred a single torsion wire.

A. Uniform rotation.

1. Rotation of a sphere. Theoretically, the most suitable form which can be selected for rotation experiments is that of an ellipsoid of revolution, in the simplest case a sphere, since there are then no edge- or end-effects to be estimated or eliminated. Assuming that the liquid rotates in concentric spherical shells, Brillouin[11] shows that a sphere of radius a, rotating with an angular velocity Ω in a liquid of viscosity η contained within a concentric fixed sphere of radius b, experiences a viscous drag equal to a couple

$$G = - 8\pi\eta\Omega \frac{a^3 b^3}{b^3 - a^3}. \qquad . \qquad . \qquad . \qquad \text{(IX. 5)}$$

To an accuracy of 0·1 per cent. it is sufficient to regard b as infinite if the walls of the container are nowhere nearer than $9a$ to the surface of the sphere: in this case $G = - 8\pi\eta\Omega a^3$. The corresponding general expressions for the couple acting on a rotating ellipsoid of revolution are quoted by Brillouin* from Kirchhoff:[12] with an infinite containing vessel the couple is

$$G = \frac{16}{3}\pi\eta\Omega \frac{a^2(a^2 - c^2)^{3/2}}{c(a^2 - c^2)^{1/2} - a^2(\pi/2 - \sin^{-1}c/a)}, \quad . \quad \text{(IX. 6)}$$

where a and c are the semi-axes of the ellipsoid.

Owing presumably to the constructional difficulties, few in-

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* *Leçons*, § 80. But in this and the following section (rotation of a disk) Brillouin's formula for the couple is wrong owing to a slip in integration. In § 82 he has also omitted a factor $1/h$ in each formula.

vestigators have made use of the above relations in designing a viscometer. Experiments with rotating spheres have been described by Élie,[13] Brodmann,[14] and, in considerable detail, by Zemplén.[15] Zemplén rotated an outer sphere of radius 5·565 cm. about a suspended hollow sphere of radius 5·007 cm. prepared by copper-plating a wax sphere and melting out the wax. With water at 18° C. he found that the deflexion ceased to be accurately proportional to the speed of rotation at speeds greater than one revolution of the outer sphere in 23 seconds. In some experiments with gases (air and carbon dioxide) in which the relation between deflexion and speed of rotation was more fully examined, he found that the deflexion at any given speed Ω was greater than that estimated for infinitely slow speed in the ratio of $(1 + 0·0069\ \rho^2/\eta\Omega^2 + \ldots)$ to unity. This empirical correction applies only to his particular apparatus: the constants would presumably vary with the dimensions (cf. Taylor's criterion for cylinders, § 3 (a)).

2. Rotation of a disk. By assuming $c = 0$, equation (IX. 6) may be applied to an infinitely thin disk, giving the very simple relation

$$G = -\frac{32}{3}\eta\Omega a^3 \quad \ldots \quad \text{(IX. 7)}$$

for a disk rotating in an infinite liquid. Brillouin shows[17] that the dimensions of the container may be taken into account approximately by dividing the expression on the right-hand side of this equation by a factor f:

$$f = 1 + \frac{2}{\pi}\left(\frac{ax}{a^2+x^2} - \frac{\pi}{2} + \tan^{-1}\frac{x}{a}\right), \quad \ldots \quad \text{(IX. 7a)}$$

where x may be taken as the half depth of a wide but shallow vessel in the median plane of which the disk rotates. Brillouin's correction is probably not applicable unless $x > a$, in which case (IX. 7 a) may be simplified, in first approximation, to

$$f = 1 - \frac{4a^3}{3\pi x^3}.$$

The container may therefore be regarded as infinite (correction less than 0·1 per cent.) if the walls are nowhere nearer than 7·5 a to the disk.

If the distance between the disk and the bottom of the container is not large compared with the radius of the disk, the distribution of velocities becomes rather different. For a disk rotating between

two fixed parallel planes, each at a distance h from it which is small compared with the radius, the couple may be shown to be, to a first approximation,

$$G = -\pi\eta\Omega a^4/h. \quad . \quad . \quad . \quad . \quad \text{(IX. 8)}$$

This expression is obtained on the assumption that the angular velocity of any layer of the liquid is a linear function of the distance of the layer from the moving disk, as it would be if the disk and the parallel planes were infinite and the rotation infinitely slow. Maxwell[18] suggested that the effect of the edge might be taken into account by assuming that the extra friction due to the disturbance of this distribution near the edge was equivalent to that which would be exerted, if the distribution remained unaltered, on an additional annulus of width $(\delta a) = 2h/\pi . \log_e 2$; supposing this force to act at the edge, the total couple becomes

$$- G = \pi\eta\Omega a^4/h + 8\eta\Omega a^3 \log_e 2. \quad . \quad . \quad \text{(IX. 8 a)}$$

Brillouin[19] considers that this correction is certainly too great and that the supplementary friction should be supposed to act at a radius nearer to $a - (\delta a)$ than to a. He shows that the additional couple due to the edge-effects is actually rather less than $\{1 - 3(\delta a)/a\}$ times that indicated by Maxwell. By supposing $x < a$ in equation (IX. 7 a) we obtain $G = -8\pi/3x . \eta\Omega a^4$, an approximation which may be compared with (IX. 8 a) to illustrate the nature of the errors involved in correcting for the effects of the container and of the edge respectively.

If the disk were suspended so as to be deflected to a steady position by the rotation of much larger disks about the same axis, the edge-effect might be reduced by the use of a fixed guard ring concentric and in the same plane with the suspended disk. If the clearance between the ring and the suspended disk is f and is small compared with h, the width of the hypothetical annulus to be added in estimating the couple exerted on the deflected disk becomes[20] $(\delta a) = f\left(1 - \dfrac{\pi}{8} . \dfrac{f}{h}\right)$. The extra couple is then $4\pi\eta\Omega a^3(\delta a)/h$ where Ω is here the speed of rotation of the two driven disks.

The Macmichael viscometer. In view of the difficulties in the mathematical treatment of the problem of the rotation of a disk in a viscous liquid the method has not been used in absolute determinations of viscosity. At any speed of rotation, moreover, the

disk would tend to act as a centrifugal pump. By rotating a cylindrical containing vessel about its axis, which coincides with the axis of suspension of the disk, there is obtained a system in which concentric rather than radial flow of liquid is favoured; to a first approximation at least, the force acting on the hanging disk may be expected to be proportional to the viscosity of the rotating
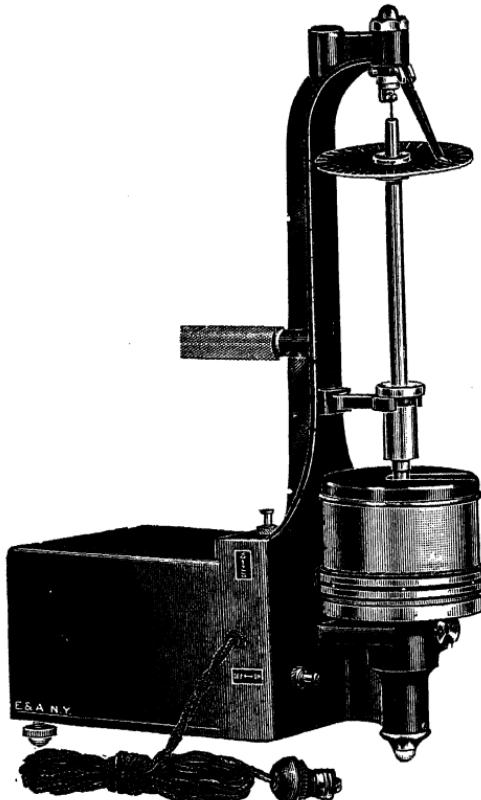
FIG. 37. Macmichael viscometer (Messrs Eimer & Amend).

liquid, in which case the 'constant' of the instrument may be determined by calibration with a liquid of known viscosity. The application of this principle to the construction of a viscometer adapted for routine work is due to Macmichael,[21] and the instrument is marketed by Messrs. Eimer & Amend of New York, from whose leaflet Fig. 37 is reproduced. A disk, of 3 cm. radius, is hung at some 5 mm. from the bottom of a cylindrical cup which is fixed in a bath on a turn-table driven at constant speed (normally 20 r.p.m.) by an electric motor and suitable gears: there is a clear-

ance of 5 mm. between the edge of the disk and the wall of the cup. The suspension wire (about 25 cm.) is enclosed in and fixed near the bottom of a tube or spindle to which the disk is fastened by a bayonet catch: the top of the spindle carries a graduated dial, the deflexion of which below a pointer indicates the twist produced in the wire when the cup containing the liquid under test is rotated. The circumference of the dial is divided into 300 equal parts, called 'Macmichael degrees'. The temperature is controlled by electrical heating. It is claimed that by using different suspension wires, from 34 to 18 B. and S. gauge, measurements may be made on liquids having viscosities from 0·6 to 2,500 poises, calibration being effected by the use of sucrose solutions or oils in the lower ranges and by a process of stepping up for the higher. A table is supplied indicating the maximum deflexion allowable for each gauge of wire so that errors due to permanent set may not occur.

Theory indicates (cf. Herschel[22]) that, if viscous forces were alone operative in producing a couple on the disk, the deflexion obtained with a given wire should be proportional to the speed of rotation of the cup and to the viscosity of the liquid. Each of these generalizations is found to be incorrect outside certain limits, and it may be shown that the criterion is a function of $\Omega a^2 \rho / \eta$, similar errors occurring at similar values of the criterion. The calibration curves determined by experiments in which Ω is kept constant are found, in fact, to be indistinguishable from straight lines only above a certain viscosity, and Herschel was able to demonstrate the effect of changes in the density of the liquid on the deflexions produced at low viscosities. The straight lines he obtained by plotting deflexions against viscosity did not pass through the origin: hence in the calibration at least two tests are required with each wire. The speeds now recommended are lower than were employed by Herschel, and liquids of viscosity less than 60 cp. are not normally examined; hence the curvature of the calibration charts near the origin appears less marked. When the thicker wires are in position, for tests on very viscous liquids, it is legitimate to assume the deflexion proportional to viscosity above a certain minimum at which the errors of observation become of the same order as those due to departure from the concentric type of flow. The instrument has also been improved in construction since the date of Herschel's tests: a special modification, based on

recommendations of the Pittsfield laboratories of the General Electric Company, is supplied for tests in which temperatures up to 150° C. are required.

3. Rotation of a cylinder.

(a) *Theory.* Imagine an infinite cylinder, of radius a, rotating about its longitudinal axis with a uniform angular viscosity Ω inside a fixed concentric cylinder of radius b, the space between them being filled with a viscous fluid. At 'slow' speeds we may expect to find that the fluid will rotate in layers concentric with the two cylinders: assuming that there is no slip, the layer in contact with the moving cylinder will have an angular velocity Ω, and that in contact with the fixed wall will be stationary. Let the angular velocity at any intermediate radius r be ω: the gradient of angular velocity being $d\omega/dr$, the gradient of linear velocity across a small element of the fluid at the circumference of the circle of radius r is $r \cdot d\omega/dr$. The viscous force exerted on the fluid inside a hypothetical cylinder of radius r and length h by the more slowly moving fluid between it and the outer wall is thus $\eta r \cdot d\omega/dr \times 2\pi rh$. About the axis of rotation this force has a lever-arm r so that the couple tending to retard the motion of the hypothetical cylinder is

$$- 2\pi\eta hr^3 \frac{d\omega}{dr} .$$

The couple G required to maintain a length h of the inner solid cylinder in rotation may be supposed measured by extraneous means: for equilibrium, we must equate the accelerating to the retarding couple at each and any radius so that

$$\frac{d\omega}{dr} = - \frac{G}{2\pi\eta h} \cdot \frac{1}{r^3} . \quad . \quad . \quad . \quad \text{(IX. 9)}$$

Integration between the limits $\omega = 0$ to Ω and $r = b$ to a gives

$$G = 4\pi\eta h\Omega \div \left(\frac{1}{a^2} - \frac{1}{b^2}\right), \quad . \quad . \quad . \quad \text{(IX. 9 a)}$$

so that η may be determined from observations of G and Ω and the dimensions of the apparatus.

The above formula was first developed by Margules[23] and has been applied by many investigators to the practical case of finite cylinders by using various expedients to eliminate end-effects. On the above simple theory it is immaterial whether the inner cylinder rotates and the outer is fixed, or vice versa: the problem being one

of relative rotation, the couple may be measured at that radius which is most convenient. For experiments on liquids of high viscosity, which will furnish a couple of several thousand dyne-cm. at moderate velocities of a small cylinder, the simplest construction is obtained by applying a known torque to the inner cylinder through a system of weights and pulleys and observing the rate of rotation after a steady state has been reached. When the torque necessary to provide a suitable speed becomes so low that the friction of the pulleys would be important, the converse design is adopted in which the outer cylinder is rotated at constant speed by a motor and the inner cylinder is suspended from a torsion wire, the deflexion of which gives a measure of the moment of the viscous forces.

Before going into any instrumental details, we may inquire at what speed of rotation the concentric type of flow above postulated will become unstable, for it is obvious that at sufficiently high speeds of the inner cylinder the viscous forces will become negligible compared with those which tend to produce radial or eddy motion of the fluid. The earliest experiments relating to this question were those of Couette,[24] who found that turbulence occurred with water and with air in his apparatus ($a = 14 \cdot 393$ cm., $b = 14 \cdot 630$ cm.) when the outer cylinder rotated at a speed given by $R_r = \Omega a (b - a)/v = $ ca. 1900. Mallock,[25] using a smaller apparatus with $a = 7 \cdot 632$ cm., $b = 9 \cdot 943$ cm., was able to reach much higher values of R_r, 4,200 to 32,000, before the laminar condition broke down. Rayleigh[26] considered that though the motion of a non-viscous fluid should be stable at all speeds of rotation of the outer cylinder about a fixed inner one, a viscous fluid would probably be unstable above $R_r = 2,100$. More recent work by Taylor,[27] with cylinders of smaller diameter ($b = 4$ cm.) and greater length than had been used previously, suggests that the turbulence found by Couette and Mallock was due to insufficient accuracy or rigidity of construction or else to incomplete elimination of end-effects, and that concentric flow may persist at all speeds. He found no instability when he rotated the outer cylinder only at the highest speed of which his apparatus was capable ($R_r = $ ca. 12,500 apparently).

When the inner cylinder rotates and the outer is fixed, Rayleigh's treatment suggests that no stability is possible for a non-viscous fluid; Mallock[25] was unable to produce concentric motion with water under such conditions. Taylor, however, analysed the

general case in which both cylinders rotated in the same or in opposite directions, and obtained a formula which reduces, for the special case which we are considering, to

$$\frac{\Omega_c^2 a^2 d^3}{\frac{1}{2}(a+b)\nu^2} = \frac{\pi^4 f}{0\cdot0571 f^2 + 0\cdot00056}, \quad . \quad . \quad \text{(IX. 10)}$$

where Ω_c is the critical speed of rotation of the inner cylinder at which turbulence appears, $d = b - a$ and $f = 1 - 0\cdot652\, d/a$. The formula was obtained on the assumption that d/a was small, but Lewis[28] found critical speeds which were in excellent agreement with it up to $d/a = 0\cdot71$. It is apparently necessary, not only that the cylinders be extremely accurately formed and truly mounted in good bearings, but also that they should have a length many times greater than their diameter: when instability arises it is three-dimensional, outward radial flow occurring at intervals of approximately $2\,d$ along the cylinders. Lewis suggests the observation of critical speeds, with the outer cylinder fixed, as a method of measuring relative viscosities which involves no determinations of torque.

For purposes of design it may be useful to evaluate the expression (IX. 10) for the case when d/a is negligibly small. Expressing the angular velocity Ω_c as $2\,\pi/t_c$, where t_c is the number of seconds per revolution when instability occurs, we obtain

$$\frac{a d^3 \rho^2}{t_c^2 \eta^2} = 43.$$

When $d = \frac{1}{2}a$, the value of the criterion increases from 43 to 78.

From dimensional considerations Hersey[29] showed that the general equation for the torque exerted on a suspended inner cylinder by a uniformly rotating outer cylinder containing liquid was

$$G = \eta \Omega\, a^3 \cdot f \left\{ \frac{\Omega^2 a}{g}, \frac{\Omega a^2 \rho}{\eta}, \text{shape} \right\} . \quad . \quad . \quad \text{(IX. 11)}$$

He considered three special cases:

(1) The inner cylinder projects above the level of the liquid and turbulence and the effect of the bottom are negligible, i.e. terms involving ρ may be ignored. A few experiments in which Ω is varied while a is constant will then enable us to determine what proportions and speed are necessary in order that the variation in wetted length due to the concavity of the liquid surface produced by centrifugal force may compensate for fluctuations of speed:

the mean torque will then be accurately proportional to the mean of varying speeds and there will be no need for a governor.

(2) If the effect of the bottom is such that though the torque is not independent of ρ, the free surface is plane at all speeds, the value of $G/\eta\Omega$ for the instrument is a function of $\Omega a^2/\nu$ only: hence, by observing, with a single liquid, what function of the speed the torque is, the instrument may be calibrated to find what function of viscosity the torque is.

(3) It is only when end-effects are negligible, e.g. when the inner cylinder is long and slender, and the speed is 'low', that the torque can be calculated as in (IX. 9 a): the requirements are satisfied if the torque is found to be proportional to speed when a given liquid is tested and therefore the torque will be proportional to the viscosity, when a given speed is maintained in tests on different liquids.

(b) *Methods of eliminating end-effects.* Formula (IX. 9 a) was deduced on the assumption that the cylinders were of infinite length. It is therefore necessary, at least for absolute measurements, to eliminate or correct for end-effects. No suitable correction has been developed mathematically, and even the form of the correction would probably be different for different geometrical shapes, but fairly successful elimination has been obtained in several different ways.

The method introduced by Couette[30] has been very generally adopted. Above and below the suspended cylinder 'guard rings', i.e. cylinders of the same diameter, are rigidly fixed so as to be co-axial with it and to allow the minimum clearance between the free and the fixed edges. Each of the guards is usually about 2/5 of the length of the suspended cylinder, so that disturbances due to the plane ends of the rotating shell of liquid are mainly confined to the space between the fixed guards and the outer cylinder. The liquid fills up the interior of the inner and guard cylinders: in order that the rotation of the base of the outer cylinder and of the free surface of the liquid may not be imparted to this column of liquid, the opposite ends of the guard cylinders are closed, except for a few necessary perforations, by horizontal plates. A diagram of the arrangement is shown in Fig. 38 where the clearances between the guard rings and the suspended and rotating cylinders have been purposely exaggerated.

The length of guard necessary varies, presumably, according to

the radial thickness of the liquid layer and the velocity of rotation. In the apparatus of Couette and in that of Gilchrist[31] the length of the guards was about 14 times the difference between the radii: in that of Leroux[32] the ratio was about 10:1. Drew,[33] who used
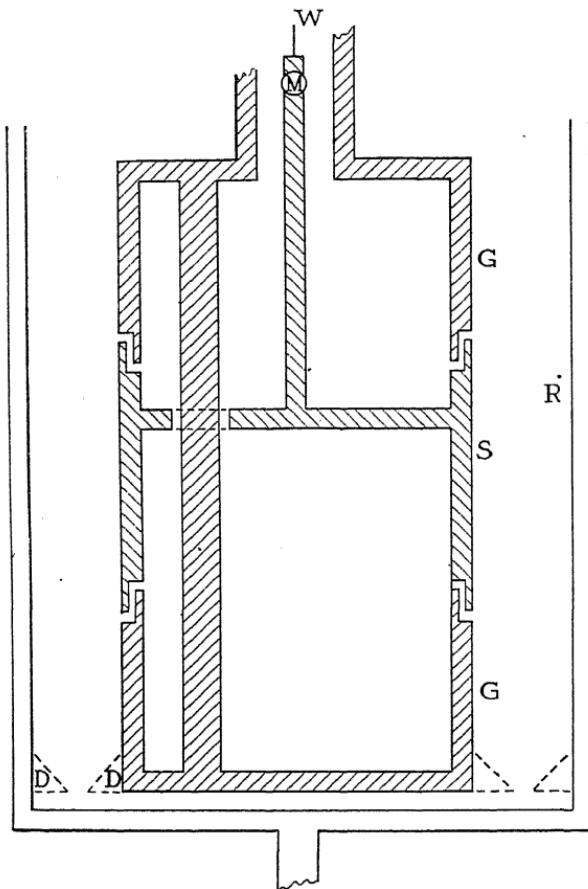
Fɪɢ. 38. Guard-ring method of eliminating end-effects.
R = rotating cylinder; s = suspended cylinder; GG = guard-rings fixed to each other and to torsion-head; M = mirror; w = suspension; DD = additions made by Drew.

rather a short guard cylinder—in one set-up apparently only about 6–7 times $(b - a)$—found that the elimination of the end-effect was considerably improved by attaching rings of triangular cross-section, as shown by the dotted lines of Fig. 38, to the outer wall of the guard cylinder and to the inner wall of the outer cylinder. The idea underlying Drew's device is that the liquid near the end

may have the speed which corresponds elsewhere with a radius $b - \frac{1}{2}(b - a)$ at approximately this same radius instead of at one nearly equal to a as would be the case without the attachments.

If the suspended cylinder is only partially immersed, the flow near the free surface of the liquid differs from that lower down merely in virtue of capillary effects: it is then chiefly necessary to eliminate the effect of the bottom. In his earlier experiments Mallock[34] trapped a shallow layer of air under the base of the inner cylinder: this does not, of course, do much towards establishing the desired velocity gradient between the vertical walls, though it removes most of the drag on the base; a similar device is incorporated in the cylindrical bob of the 'Improved Macmichael' viscometer (*vide infra*). Mallock's second apparatus[35] included a short guard-ring between which and the outer cylinder a layer of mercury was poured to reduce the drag at the bottom of the annular cylinder of water under test. More recently Weinberg[36] has also made use of mercury to cover the pivot and lower end of an inner cylinder rotating in an outer one for tests on pitch, &c.

Instead of, or in addition to, such mechanical contrivances, a differential method may be used to eliminate or to estimate the end-effects. If, as in Drew's apparatus, the suspended cylinder is not completely immersed, variation of the height of the liquid will vary the length of the cylinder on which the viscous forces can act, and if the end-effects were negligible the torque produced would be proportional to the wetted length: from the lack of proportionality the importance of the disturbance may be estimated. This method has recently been applied by Lillie.[37] Searle's viscometer[38] was so designed that the working volume of the liquid need not be varied: the inner cylinder (Fig. 39) is the rotating member and the wetted length may be varied by raising or lowering the outer cylinder. For this purpose there is attached below the base of the outer cylinder a sleeve which fits, and may be clamped at any desired height, on the pillar that carries the lower bearing for the spindle of the inner cylinder: a perforated plate fixed to the top of the pillar acts as a false bottom the position of which is constant. Assuming that the effects of the curved liquid surface near the top and of the plane end at the bottom of the rotating cylinder are equivalent to a virtual increase l in the wetted length h, the couple produced by a given rate of rotation of a given liquid should be proportional to $h + l$. More generally, since G/Ω must be constant.

(cf. equation IX. 9 a) for a given filling if the above assumption is justified, G/Ω should be proportional to $h + l$. A scale is provided on the inner cylinder so that h may be read when the outer cylinder has been clamped in various positions. Values of G/Ω are obtained, each from several observations at different speeds of rotation, for a series of different values of h, and the results are plotted: the straight line drawn through the points is extrapolated to cut

Fig. 39. Searle's viscometer (Messrs. W. G. Pye & Co.).

the h axis beyond the origin and the intercept is taken as equal to $- l$. With $b = 2 \cdot 54$ cm. and $a = 1 \cdot 86$ cm., Searle found $l = 0 \cdot 55$ cm. in an experiment with syrup having a viscosity of 1,420 poises.

If the inner cylinder is totally immersed Searle's method is not applicable, but a similar principle was used by Gurney,[39] who made observations of the couple exerted on each of two suspended cylinders of the same radius ($a = 4 \cdot 5$ cm.) but of different lengths, when an outer cylinder ($b = 5 \cdot 6$ cm.) was rotated at a given speed. The suspended cylinders had lengths of 5 and 10 cm. respectively and had plane ends. They were adjusted so that their bases were 5 cm. from the bottom of the outer vessel: the level of the water under test was set in each case at 5 cm. above the top of the inner cylinder. The length of the shorter cylinder in Gurney's experiments does not appear, however, to have been a sufficient multiple of the clearance between it and the outer cylinder to warrant the

assumption that end-effects were negligible over any portion of the vertical surface.

The success of any of the above methods in eliminating turbulent end-effects may be compared by noting the angular velocity up to which the ratio G/Ω remains constant for a given pair of cylinders: but purely viscous forces near the ends may also modify the distribution of velocities in the remoter strata. The occurrence of such modification is probably most readily detected by some method like Searle's, since the failure of the linear relationship between G/Ω and h indicates the value of h at which the disturbance, of whatsoever nature, is first sensible.

(c) *Outer cylinder rotated, inner cylinder suspended.* We have seen that though on the simplest theory it is immaterial to the magnitude of the viscous couple which of two concentric cylinders is rotated, there is a great difference between the stability of the alternative arrangements. With given dimensions it is possible to employ much higher angular velocities when the inner cylinder is stationary; for experiments on liquids having viscosities of a few centipoises, and particularly for work with gases where the torque produced at low speeds would be very low, this disposition is almost essential and it has been adopted in the majority of the viscometers which have been constructed on the rotating-cylinder principle.

In order to minimize the effect of errors arising from lack of coincidence of the geometrical axes of the two cylinders and of their axes of rotation, it is desirable that the clearance between the vertical surfaces be large. Errors of figure and of measurement of radius tend to be increased as the radius is decreased below a certain limit, but if the clearance is large the highest precision in the construction and in the determination of dimensions is required only for the inner cylinder. Couette showed by analysis that if the eccentricity were equal to $m(b-a)$, the relative error in the estimation of viscosity by equation (IX. 9 a) would be $\frac{1}{2}m^2$ to a first approximation. Gurney[39] found experimentally that the difference in torque caused by displacing the axis of his inner cylinder ($a = 4\cdot50$ cm.) by 1 mm. from that of the outer ($b = 5\cdot57$ cm.) amounted to 0·18 per cent. But as the clearance is increased, the torque produced by a given rate of rotation is decreased so that more sensitive suspensions are required. Limitations are imposed,

not only by the difficulty of obtaining a strong suspension of adequate sensitivity, but also by the desirability of making the natural period of oscillation of the system short. When a torsion wire is used as the suspension, this period is given by equation (IX. 2): for a bifilar suspension equation (IX. 4) applies. If the period is long, the deflection produced by rotation will not immediately reflect any inconstancy of speed, and the mean reading may be difficult to estimate when the oscillations are serious. Hersey[40] considered it to be essential that the period be short and his own instrument had a time of vibration of 5 secs., but in Harrington's adaptation[41] of Gilchrist's apparatus[42] periods up to 176 seconds were successfully employed—with a good driving motor—by arranging to start and stop the drive gradually. In the Macmichael viscometer a dash-pot is provided to damp the oscillation when the lighter suspensions are mounted for tests on liquids of low viscosity.

Few absolute determinations of viscosity have been made by the rotating-cylinder method for which any very high degree of accuracy can be claimed. Couette himself obtained a value for water 14 per cent. higher than that accepted and did not profess to have discredited the latter. The only important absolute measurements appear to be those of Gilchrist[42] and of Harrington[41] on air and those of Leroux[43] on water. The apparatus used by each of these investigators was of the same type as that of Couette, i.e. it included guard cylinders for the elimination of end-effects as shown diagramatically in Fig. 38. But the precision attained in their final results necessitated an extremely high degree of skill in the construction and the most minute precautions in the various adjustments of the apparatus. The full descriptions given cannot be reproduced here—the paper of Leroux contains no less than twenty-seven diagrams and three photographs, and details would not be intelligible in a brief abstract. It may be well to mention that Leroux lays great stress on the necessity of designing the apparatus so that the guard cylinders are accurately concentric with the outer cylinder, a condition which he realizes by attaching them rigidly to an outer sleeve carrying the conical bearings for the upper and lower ends of the rotating member.

Slight inaccuracies in construction and incomplete elimination of end-effects are of less importance in rotating-cylinder viscometers intended for relative measurements. Such faults will mainly operate to reduce the maximum angular velocity which is

attainable before the deflexion ceases to be proportional to speed, i.e. begins to be dependent on the density instead of on the viscosity only. The apparatus of Hatschek[44] has been used, by himself and his collaborators as well as by Freundlich and his school, chiefly for the examination of the effect of rate of shear on apparent viscosity. For such purposes it is the lower speeds which are of most interest and the graph of the relation between G and Ω shows a curved portion near the origin, in the case of anomalous liquids, which is quite clearly separated—usually by a straight line of considerable length—from the 'break' due to turbulence which occurs at the highest speeds. Hatschek found that with his first apparatus the viscosity of water appeared to increase with rate of shear, indicating that the effect of the ends was not eliminated by the short guard cylinders EE^1 (Fig. 40) placed above and below the hollow suspended cylinder A. Extension of the base of the lower guard cylinder by means of the thin plate H, reaching to within 1 mm. of the wall of the rotating cylinder, improved the elimination so that the apparent viscosity of water now increased by only 1 per cent. when the angular velocity was increased fivefold: but a diagram given by Humphrey and Hatschek for a toluene-carbon tetrachloride mixture of specific gravity 1·50 at 13° C. shows an increase in apparent viscosity of 12 per cent. for a change of speed from 20° per sec. to 130° per sec. The outer diameter of the suspended cylinder was 10 cm. and the clearance between this and the rotating cylinder was 0·5 cm.: the length of the guard cylinders was apparently less than four times this clearance and should be increased for critical experiments in liquids of low viscosity. The guard cylinders were supported by three rods from the centring head at the top of the bracket C and passed through slots (shown in the inset) in the horizontal plate of the suspended cylinder: the deflexions were read by means of the mirror G with a telescope and scale.

The Macmichael viscometer (see Fig. 37) is supplied not only with a suspended disk but alternatively with cylindrical bobs of 1, 2 or 3 cm. diameter, to be used with containing cups of either of two diameters. The effect of the bottom of the cup is partially eliminated by the trapping of an air bubble under the bob, but no guard cylinders are included. The omission of guards simplifies not only the construction but the operation, and particularly the cleaning of the viscometer, which has consequently found considerable

application in the examination of varnishes, starches, and other colloidal solutions. Herschel[45] showed that in tests of liquids having viscosities above about 50 cp. turbulent end-effects were negli-

Fig. 40. Hatschek's viscometer (from Hatschek,
The Viscosity of Liquids).

gible compared with the errors due to set of the wires. The calibration curves at the low speeds now recommended are straight lines, within the experimental error, except at the lowest viscosities. The errors due to set arise chiefly from the use of the large deflexions necessitated by the method of reading. At the higher viscosities such errors become small compared with those caused

by variations of temperature, and the Macmichael apparatus is the only one of this type in which provision is made for regulation of the temperature by means of a heated bath rotating with the outer cylinder.

(d) *Outer cylinder fixed, inner cylinder rotated.* The design and construction of viscometers of the type here considered are simpler in many respects than for those described in (c). The inferior stability of the present arrangement (cf. § 3 (a)) together with the fact that it has not been convenient to measure the torque by any more sensitive means than a weight and pulley, have practically restricted its use—for absolute determinations—to the examination of liquids having viscosities of more than say, 50 poises. In practice, a known turning moment is applied to the inner cylinder and the rate of rotation is observed when a steady condition has been reached, i.e. when the viscous drag on the rotating cylinder has become equal to the applied torque. The torque being equal to WR, where W is the tension in a wire or thread tangential to the circumference of a pulley wheel of radius R which turns on the same axis as the rotating cylinder, equation (IX. 9 a) becomes simply

$$\eta = \frac{WR}{4\pi h\Omega} \cdot \frac{b^2-a^2}{(b^2-a^2)^2} \cdot \quad . \quad . \quad . \quad (IX.\ 12)$$

The first practical viscometer operating on this principle was that of Searle:[46] the design and use of this apparatus have already been described (Fig. 39 and p. 227) in connexion with the method of elimination of end-effects. Searle found that the product Wt (where t is the time of one revolution) was constant for any given level of a given liquid—he examined black treacle and golden syrup—so long as the wetted length of the inner cylinder was not too short. As might be expected, the value which he obtained for the viscosity of water was excessive (nearly 19 per cent. too high) owing to effects of turbulence. In a series of experiments with treacle Molin[47] thought he had detected a variation of viscosity with rate of shear, the product Wt tending towards infinity for small values of W, i.e. at low speeds. Lewis[48] showed, however, that Molin's results for each wetted length of inner cylinder gave a straight line when W was plotted against $1/t$; the straight line did not pass through the origin when it was extrapolated to zero speed, but intersected the W axis at a positive value of W. The

relations may be explained by assuming that the intercept w multiplied by R is the couple which is required to overcome the friction in the bearings, the viscosity being constant and proportional to $(W - w)t$ instead of to Wt. The value of w was found to vary slightly with the depth of immersion of the rotating cylinder, i.e. with the load on the lower pivot: it differed considerably from that estimated from the rates at which the cylinder rotated in air when small loads were applied.

In viscometers which are to be used for purely relative measurements, being calibrated—if desired—by means of liquids of known viscosity, elimination of end-effects is unnecessary except in so far as these effects are due to properties other than viscosity, e.g. to surface tension or to density. Variations of surface tension between pure liquids have not been shown to cause error in rotation experiments, but several investigators have commented on the occurrence of a 'surface rigidity' which appears to have been due in some cases to corrosion of a brass apparatus by water[49] and in others to the formation of a skin by the exposure of the liquid to air.[50] In contrast with viscometers in which the outer cylinder is rotated, so that the average angular velocity of the liquid is greater at the ends than near the middle of the cylinders, the rotation tends to be damped below a cylinder which is rotated inside another: forces proportional to density acting near the ends do not appear likely to cause error, in viscometers of the type here considered, until forces of the same nature become important in planes near the median. In few of the numerous descriptions of 'relative' viscometers designed with a rotating inner cylinder has any attempt been made to eliminate end-effects except by making the cylinder long in relation to its diameter. Weinberg,[51] however, gives an illustration of an apparatus used by Smirnow and himself in a study of the viscosity of pitch, in which the lower bearing and the bottom of the inner cylinder are immersed in a pool of mercury on which the pitch rests.

The principle has been applied by several workers to the determination of the viscosity of molten silicates, particularly of glasses: reference may be made to papers by Feild,[52] by Washburn,[53] by English,[54] by Stott, Irvine, and Turner,[55] and by Gehlhoff and Thomas.[56] The most recent is that by Proctor and Douglas[50] already cited: these authors caused a sillimanite rod, ground for a length of 7·5 cm. to a diameter of 0·97 cm., to rotate in molten

glass contained in a fixed pot of 4 cm. internal diameter, the depth of immersion being 4·5 cm. The top of the rod was fitted, outside the furnace, into a sleeve which was attached to a bicycle axle so that the rod could rotate truly: the upper end of the axle carried a horizontal pulley of 11 cm. diameter, on the circumference of which was wound a fine wire passing over a vertical pulley and carrying loads varying from 4 to 2,000 gm. The temperature was measured by a thermocouple embedded in the rod, the temperature of the glass in contact with the rotating member (where the rate of shear is greatest) being of more importance than the average temperature. The large ratio between the diameters of the pot and of the rod is rendered possible by the order of viscosities to be measured (10^3 to 10^9 poises) and has the effect of reducing the error produced by inaccurate centring of the rod with respect to the axis of rotation or the axis of the pot. The friction of the rotating system was equivalent to a load of 1·5 to 1·8 gm., and was sufficient to cause considerable error only in tests at viscosities below about 1,000 poises. At the highest speeds of rotation, in syrup used for calibration purposes, a definite indication of the onset of turbulence was observed in the Ω, W diagram. The viscosity of the syrup (265 to 524 poises) was determined by the falling-sphere method; that of pitch ($0·68 \times 10^8$ to $1·91 \times 10^8$ poises), which was used to provide a check on the calibration factor obtained with syrup, was measured by a method due to Trouton and Andrews (see Chap. X, § D).

A viscometer of the same type, which has been used in many technical investigations, is that of Stormer,[57] which, though at first made with a flat stirrer for tests on plastic materials, is now supplied with a cylinder rotating in a cylindrical cup. The outer vessel shown in Fig. 41 (reproduced from the leaflet of Messrs. Arthur H. Thomas Company of Philadelphia) is a water- or oil-bath for regulation of temperature: the cup containing the liquid under test is fixed centrally in this. The hanging weight turns the large gear wheel which engages with a pinion on the shaft of the rotated cylinder: the number of revolutions of the latter is indicated by a counter. For liquids having viscosities below 50 cp. a 100 gm. weight is used and the time for 100 revolutions is observed: for work on the consistency of pastes, &c., the water bath and cup are replaced by a large can and the rate of revolution is further increased by using a 750 gm. weight. The regular cup is provided

with two vanes, projecting radially inwards towards the rotating cylinder, and with a central baffle to increase the resistance when viscosities below 50 cp. are in question: the central baffle may be omitted for tests on liquids of higher viscosity.

The presence of the vanes must considerably modify the flow of the liquid between the two cylinders from that postulated in the derivation of equation (IX. 9 a): the liquid is accelerated on
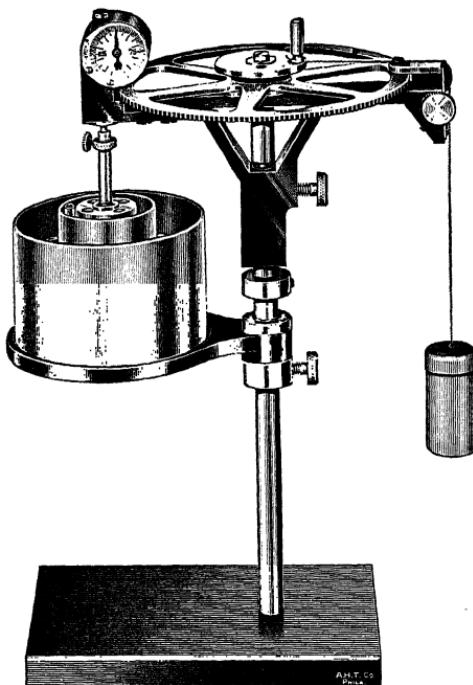
Fig. 41. Stormer viscometer (Messrs. Arthur H. Thomas Co.).

one side of a vane and decelerated on the other side; the baffle is an additional complication to the theory. Further, the rate of rotation when using a 100 gm. weight in a water test is so high that the flow of water would not be purely viscous: it is not, therefore, accurate to determine a factor for conversion of the rate of revolution to absolute viscosity by means of a single calibration with water. The makers suggest that a lower driving weight be used to find the relative resistances offered by water and by an intermediate standard, and that a heavier weight be then substituted when comparing the intermediate standard with a more viscous liquid. Besides confining the rates of rotation to a narrower

range for convenience of observation, such a procedure will tend to diminish the importance of the forces involving the density of the liquid.

The behaviour of the Stormer viscometer has been examined by Rigg and Carpenter[58] and by Higgins and Pitman.[59] Neither of these investigations was much concerned with the effect of the forces due to turbulence, but in both some effort was made to eliminate errors arising from friction in the rotating system. Rigg and Carpenter simply deducted the time for 100 revolutions in air from the observed times for 100 revolutions in each liquid tested and found that this gave better concordance between the time ratios obtained when different loads were used. Higgins and Pitman wrote $\eta = At - B$ where A and B are constants differing according to the load used (150 or 300 gm.): the relation between η and t was not linear, however, for viscosities below 15 cp. By analogy with the result found by Lewis for the Searle viscometer (p. 233) it is probable that, over the range of viscosities in which the relation between speed and torque is linear, the constant A should be proportional to $W - w$ where W is the applied load and w is the equivalent of the friction in the bearings and in the gear. The second term of Higgins and Pitman's equation might be expected to contain a factor $1/t$ and to represent the effect of forces due to inertia; in this case it would also contain the factor ρ, and might be applicable even at the higher speeds, but I have not tried to fit an equation of the form suggested to the data given in their paper. The friction will naturally vary with the precision of construction and with time; the machine work is stated to be more accurate in the 'Improved Model' now supplied. The complete absence of forces due to eddy motion appears most probable in tests on liquids having viscosities so high that a large cup without vanes may be used: if the vanes were omitted in the instrument illustrated in Fig. 41, the cup would have to be of slightly smaller diameter to give a viscous couple of the same magnitude as that at present obtained. The instrument has found its chief application in the study of the consistency of plastic materials, e.g. in the silicate, paint, pyroxylin and starch industries, rather than in the measurement of relative viscosities below 1 poise: for use with highly viscous liquids or suspensions the simplicity of operation and the accessibility of the parts for cleaning are important advantages.

B. Oscillational Viscometers.

In certain circumstances the simplicity of the design of viscometers in which a suspended body vibrates about an axis of symmetry is a recommendation sufficient to outweigh the theoretical disadvantages of such apparatus. When a liquid of which any property is to be measured is at a very high or very low temperature, ease of reduction of observations has often to be sacrificed to ease of construction or of operation. From the historical standpoint oscillational viscometers are of the highest importance, since much of the development of our modern views on the nature of viscosity is due to the classical work of Coulomb, Meyer, and Maxwell, who made use of simple forms of torsional pendulum apparatus. Even to-day similar methods of measurement have been adopted as the most generally suitable for the determination of the viscosity of vapours.

1. Outline of theory. Suppose that we have a torsional pendulum consisting of a bob, which has a moment of inertia I about an axis of symmetry, suspended in a viscous medium by a wire lying along that axis. Let the couple required to twist the wire through an angle α be $M\alpha$. In the absence of viscous forces (cf. equation IX. 2) the pendulum, when displaced from rest, would execute a simple harmonic motion with a period $T_0 = 2\pi\sqrt{I/M}$. When the motion is not too highly damped by forces proportional to the velocity, the differential equation becomes

$$I_1 \frac{d^2\alpha}{dt^2} + L\frac{d\alpha}{dt} + M\alpha = 0, \quad . \quad . \quad . \quad \text{(IX. 13)}$$

where $- L . d\alpha/dt$ is the moment of the viscous forces and I_1 differs from I only by the 'carried mass' due to the inertia of the fluid. It is known that this equation is satisfied for the pendulum by

$$\alpha = Ae^{-\delta\frac{t}{T}}\cos 2\pi\frac{t}{T}, \quad . \quad . \quad . \quad \text{(IX. 13 a)}$$

where α is the amplitude of the deflection at any time t, T is the new time of vibration and δ is called the logarithmic decrement of the amplitude for one complete vibration. The experimental method consists in the estimation of δ from the ratios of the amplitudes of successive vibrations, together with a determination of the period T. When I and M are known, the problem is then to relate δ and T to the viscosity of the medium. At low speeds,

the fluid may be supposed to be divided into shells homofocal with the suspended body, which oscillate with the same period but with phases and amplitudes differing from that of the pendulum in virtue of the inertia of the fluid. The couple acting on the pendulum owing to the motion of the fluid will then involve not only terms proportional to viscosity, $-L.d\alpha/dt$ in equation (IX. 13), but also terms proportional to the density and accelerations of the fluid. By postulating certain simple boundary conditions, including the shape of the oscillating body, it is possible to obtain an expression for the motion at any point in the fluid and hence for the motion of the fluid in contact with the pendulum: by integration, the total couple due to this motion may be evaluated. The constants of the usually complicated integral involve not only the dimensions of the oscillating body and of the container, but also T, η and ρ. Now it follows from the form of equations (IX. 13 and 13a) that the real part of L is equal to $2I\delta/T_0$ when δ is small: by equating this to the corresponding constant in the expression for the couple, we obtain a relation between δ and the characteristics of the fluid and of the apparatus, from which η may be calculated when numerical values are known for the density of fluid, for the dimensions of the apparatus and for the times of vibration in the presence and in the absence of viscous effects. The relation is generally of such a form that it cannot be solved to give a direct algebraic expression for η (in the case of an oscillating sphere, for example, it is of the fourth degree in $\sqrt{\eta}$), but a method of successive approximation must be used.

Verschaffelt[60] points out that the assumption that the fluid moves in layers, which is made in arriving at the expression for the reaction of the fluid on the oscillation, requires that ω^2 should be negligible ($\omega =$ angular velocity of any layer) compared with $d\omega/dt$ and that the maximum amplitude should be a very small fraction of a radian. He found experimentally that the graph of $\log \alpha$ against time was distinctly curved at the higher amplitudes, suggesting that the oscillation was in reality a compound damped harmonic one of the form

$$\alpha = a_1 e^{kt} + a_3 e^{3kt} + a_5 e^{5kt} + \ldots ;$$

for this conclusion he was able to obtain theoretical support. Though numerical calculation was impossible for the general case, he showed how the coefficients a_1, a_3, a_5 . . . found from

experiments with certain calibrating liquids, using large deflexions, could be utilized by designing the oscillating system to give similarity of motion. With an immersed body of given form similarity of motion of two fluids requires that $\eta T/\rho R^2$ and $\eta R^3 T/I$ should be the same in the two cases, where R is a characteristic length (e.g. radius of a sphere): the two requirements may be expressed physically by saying that neither the wave-length of the disturbance in the fluid nor the logarithmic decrement of the oscillation must be changed. The period and the decrement may be adjusted by modification of the added moment of inertia and by variation of the suspension: if R is fixed, the new values both of I and of M required to give similarity of motion are fixed, for each change of fluid, i.e. of η and of ρ, by the above criteria.

2. Elimination of accessory frictional effects. In addition to the damping due to the viscosity and inertia of the fluid in which the oscillating body is suspended there are always some extraneous frictional effects produced by the motion of the other parts of the system. The air, or other gas, in contact with the suspension, with the mirror or pointer and with the masses added to increase the moment of inertia, exerts a drag on the oscillation and there is also some friction or elastic hysteresis in the suspension itself. In some cases these accessory effects constitute an important fraction of the whole damping and must be estimated accurately or eliminated. Several methods have been used:

(a) Theoretically, the most satisfactory procedure is that used by Zemplén[61] and by Verschaffelt and Nicaise,[62] in which the bob is removed altogether. Since it is necessary that the period of oscillation should be the same as in the test proper, the oscillating system includes a cylindrical annulus supported above the level of the liquid; when the bob is taken away, this cylinder is replaced by one which has the same shape, but is made of heavier material so that the total moment of inertia may be unchanged. The shape of the annuli is so selected that the total load may also be unchanged, in order not to modify the properties of the suspension. The corrected logarithmic decrement is the difference between the decrements observed in the test and in the 'blank' experiment. This method has the practical defect that since the weight of the oscillating system is more than twice that of the bob alone, the

torsion wire has to be stronger and therefore stiffer than may be convenient.

(b) In his first experiments with oscillating disks (1865) Meyer observed the logarithmic decrement of a system composed of three similar disks mounted axially on a rod, first when they were separated by a few centimetres from one another and then when they were in contact: the difference between the two results, for six surfaces and for two surfaces, was supposed to be equal to that which would have been obtained with two disks in the absence of external friction. Brillouin[63] shows that the separation between the two disks would need to be much greater than it was in Meyer's experiments before the three disks could be regarded as beyond each other's range of influence. A similar principle was employed by Maxwell (1866) under conditions such as to justify the assumption that the separated disks were independent.

(c) An alternative method used by Verschaffelt[64] consists in making a second observation of the logarithmic decrement of the torsional pendulum when it is transferred from the liquid under test into a fluid of much lower and known viscosity. The same method has been adopted by Dantuma[65] to avoid the inclusion of accessory cylinders. If the logarithmic decrements found be δ_1 when the bob is in the liquid and δ_2 when it is in air, and δ_3 be that calculated by the appropriate equation for the effect due solely to the viscous friction of the air on the bob, then the corrected logarithmic decrement δ to be used in calculating the viscosity of the liquid is equal to $\delta_1 - (\delta_2 - \delta_3)$.

In a recent study of the relative viscosities of vapours, Braune, Basch and Wentzel[66] estimated the internal friction of the suspension by noting the logarithmic decrement when the apparatus was evacuated as completely as possible. Their oscillating system, a disk between two fixed disks, did not include a mirror or other added moving surface of appreciable area, so that the only parasitic resistance was that due to the elastic defects of the quartz fibre suspension. A similar method had been used by Vogel[67] for an apparatus of the same type, which, however, included a mirror and a small astatic pair of magnets for starting the oscillation: the sum of the gaseous friction on these accessories plus the friction in the wire was calculated from two pairs of experiments in air at different temperatures with two disks having different radii but the same moment of inertia.

3. Oscillation of a sphere. The problem has been investigated theoretically for various speeds and boundary conditions by Stokes, by Helmholtz and Piotrowski (1860), Lampe (1866), König (1887), Brillouin (1907), Zemplén (1906 and 1909), and more recently and fully by Verschaffelt,[68] who gives a formula more suitable for computation than those of earlier workers:

When a sphere of radius R oscillates in an infinite fluid and constitutes (or forms part of) a torsional pendulum having a moment of inertia I and a period, when undamped, T_0, a rough estimate of the viscosity of the liquid may be obtained from the new period T by means of the relation

$$\sqrt{\eta} = \frac{3}{2} \frac{(T-T_0)\,I}{T_0{}^2 R^4} \cdot \sqrt{\frac{T}{\pi\rho}}. \quad . \quad . \quad . \quad \text{(IX. 14)}$$

Using this or a known approximate value for η, calculate

$$b = \sqrt{\frac{\pi\rho}{\eta T}} \qquad \text{and} \qquad p = \frac{bR+1}{(bR+1)^2+b^2R^2},$$

and solve for $\sqrt{\eta}$ in the quadratic equation

$$(2+p)\,\eta + R\sqrt{\frac{\pi\rho}{T}} \cdot \sqrt{\eta} - \frac{3}{4} \cdot \frac{\delta}{T_0} \cdot \frac{I}{\pi R^3} = 0, \quad . \quad \text{(IX. 14 a)}$$

where δ is the logarithmic decrement (corrected for accessory frictional effects). With this second approximation for η correct the values of b and p and again solve the quadratic equation; if δ is not extremely small it is necessary, in the final approximation, to modify the last term of equation (IX. 14 a) by substituting $\delta\{1 + \frac{1}{2}(\psi^2 - \chi^2)\}$ for δ, where $\psi = (T - T_0)/T_0$ and $\chi = \delta/2\pi$.

The fluid may be regarded as unbounded if it is contained in a vessel so large that the train of disturbances due to the oscillation is damped to a negligibly small amplitude before it reaches the wall. If the container is a concentric sphere of radius R', this condition requires that $e^{-b(R'-R)}$ be negligible compared with unity: Verschaffelt points out that this does not involve large values of b or of $R' - R$, e.g. when $\eta/\rho = 0\cdot01$, $R'-R = 1$ cm. and $T = 3\cdot1$ secs., giving $b = 10$, the criterion becomes $1/20,000$.

Equation (IX. 14a) may be simplified if $bR\left(= R\sqrt{\dfrac{\pi\rho}{\eta T}}\right)$ be either very large or very small. In the former case, e.g. for a sphere of

radius 10 cm. oscillating with a period of 0·3 sec. in an unbounded liquefied gas for which $\eta/\rho = 0·004$, with δ small,

$$\delta = \frac{4}{3}\frac{\pi R^4}{I}\sqrt{\pi\rho\eta T_0} = \frac{2\pi}{T}(T-T_0). \qquad \text{(IX. 14 b)}$$

But Verschaffelt doubts whether the derivation holds for the high velocities involved.

If bR is very small and the fluid is so bounded that $b(R'-R)$ is also small, conditions which might have been fulfilled in Zemplén's experiments[69] if a few modifications had been made,

$$\delta = \frac{4\pi}{I}\cdot\frac{R'^3 R^3}{(R'^3-R^3)}\cdot\eta T = \frac{2\pi}{T_0}\sqrt{T^2-T_0^2}, \qquad \text{(IX. 14 c)}$$

Zemplén recalculated the formula applied to the above experiments and gave a correction in an appendix to his paper on the rotating sphere,[70] but the arrangement he adopted requires very complicated formulae.

A form of viscometer which is at least of historical interest is that in which a hollow sphere is filled with the liquid and oscillates about a diameter. From an inadequate treatment of data obtained in an experiment of this nature Helmholtz and Piotrowski[71] concluded that slip occurred at the liquid-solid surface. If e^{-bR} is very small, so that the wave-motion is damped out before it reaches the centre of the sphere, the solution is of the same form as (IX. 14 a) except for some necessary changes of sign which lead to

$$(q-2)\,\eta + R\sqrt{\frac{\pi\rho}{T}}\cdot\sqrt{\eta} - \frac{3}{4}\frac{\delta}{T_0}\cdot\frac{I}{\pi R^3} = 0, \qquad \text{(IX. 14 d)}$$

where $\qquad q = (bR-1)\div\{(bR-1)^2+b^2R^2\}.$

If bR is so large that the motion is completely extinguished very near the surface of the sphere, equation (IX. 14 b) is again applicable. If bR is extremely small, e.g. for a very viscous liquid in a small sphere, the sphere oscillates as if it were solid, having its actual moment of inertia increased by $8/15$. $\pi\rho R^5$.

The practical details of construction of an oscillating sphere viscometer to which equation (IX. 14 a) shall be applicable are chiefly concerned, when the dimensions have been selected to make δ and $e^{-b(R'-R)}$ small, with the mechanical and thermal properties of the materials of which it is to be made. For experiments on liquid air ($\eta = 0·16$ cp., $\rho = 0·9$ gm./cm.³) and other liquids having viscosities up to 2·8 cp., Verschaffelt used a brass sphere of 3·85 cm. diameter; into this was screwed a steel pin of 1 mm. diameter

which was attached, via a small copper tube, to a 25 cm. glass tube serving for thermal insulation. To the upper end of the glass tube was soldered a copper tube carrying the mirror and a disk to support the cylindrical annuli of copper or of aluminium (4·4 cm. high, radii 1·74 cm. external, 0·52 cm. internal) used in connexion with the determination of accessory frictional effects. The ends of the suspension, 60 cm. of 0·17 mm. diameter phosphor-bronze wire, were soldered to copper rods screwing into the top of the oscillating system and into the torsion head respectively. The liquid was contained in a spherical shell of diameter 5·84 cm. made in two halves, the upper of which was prolonged by a tube of 2 cm. diameter: the level of the liquid reached just into this tube, so that the steel pin supporting the brass sphere protruded from the liquid. The oscillating sphere had a mass of 251 gm., the time of vibration was about 21 secs. and the logarithmic decrement in liquid air was 0·04: the maximum deflexion normally used was 4° (= 20 cm. on a scale at 1·5 metres).

For tests on liquid hydrogen the friction in the wire of the system just described was found to form too large a proportion of the total damping. The brass sphere was therefore replaced by a glass bulb of 4 cm. diameter, sealed via a glass tube to a copper tube and disk as before, but the system now weighed only 26·5 gm.: with an added annulus of 7 gm. and a manganin suspension wire of 0·04 mm. diameter the period was 40 secs. and the logarithmic decrement in liquid hydrogen was 0·10, of which one-tenth was due to friction in the wire, &c.

Dantuma[72] adapted the method for experiments on fused salts. His suspended system consisted of a platinum sphere of 2 cm. diameter, joined by 2 cm. of 1·5 mm. diameter platinum wire to a length of 4 mm. diameter nickel rod sufficient to protrude from the furnace. Over the junction of the nickel and platinum a shallow bored cylinder was placed to increase the moment of inertia. The fused salt was contained in a platinum cylinder 5 cm. in diameter and 7 cm. high. The period of oscillation was 8 secs.: the gross logarithmic decrement was 0·02 when the sphere was immersed in water at room temperature.

4. Oscillation of a disk.

(a) *Oscillation in an unbounded fluid.* If the effect of the walls of the containing vessel on the oscillation of a disk is to be made

negligibly small, the vessel needs to be very large (cf. Brillouin[73]), e.g. to have a radius $2a$ and a depth a if a is the radius of the disk and $a(\pi\rho)^{\frac{1}{2}}(\eta T)^{-\frac{1}{2}}$ is large (Kobayashi[74]). More important than this experimental inconvenience is the fact that the calculation of the relation between the logarithmic decrement and the viscosity has not yet been made with sufficient exactness to allow the method to be used even for relative measurements without the determination of at least three instrumental constants. Coulomb (1801) made experiments by this method which are very important historically, but Meyer (1861) first obtained an approximate analytical solution which may be written

$$\delta = \frac{\pi a^4 \sqrt{\pi\rho\eta T}}{2\sqrt{2}\,.\,I} + \frac{\pi a^3 \eta T}{I} \quad \cdot \quad \cdot \quad \cdot \quad \text{(IX. 15)}$$

of which the second term represents an edge correction. König (1887) showed, however, that the effect of the liquid outside the cylinder of which the disk is a cross-section required the subtraction of an inertia-term which is equivalent to $3/16\,.\,\pi^2 a^8 \rho\eta T/I^2$. The calculation has recently been repeated by Kobayashi[74] by a method which allows repeated approximations to be made: he gives the formula

$$\delta = \frac{\pi a^4 \sqrt{\pi\rho\eta T}}{2\sqrt{2}\,.\,I} + \frac{1\cdot05\,\pi a^3 \eta T}{I} - \frac{\pi^2 a^8 \rho\eta T}{4I^2}, \quad \text{(IX. 15 a)}$$

but finds that even this solution does not cause Meyer's experiments to lead to correct or consistent values for viscosity.

An equation of the type of (IX. 15 a) was applied by Fawsitt[75] and by Lorenz and Höchberg[76] to the oscillations of platinum ellipsoids of horizontal diameter 26 mm. and vertical diameter 1 to 5 mm. The constants of the three terms involving $\sqrt{\rho\eta}$, η and $\rho\eta$ were obtained by calibration with water, chloroform, and mercury (or isobutyl alcohol). Fawsitt did not claim any higher accuracy than 5 per cent. for his viscosity results: the chief virtue of the method is its comparatively ready applicability to high-temperature conditions.

(b) *Oscillation between two fixed plates.* The nature of the fluid motion is much better defined under the conditions used by Maxwell,[77] who provided a fixed disk above and below the oscillating disk. Such an arrangement minimizes the oscillation of the cylindrical annulus of fluid external to the moving disk and allows the problem to be treated, in first approximation, as

though the disk were infinite, the edge-effect being separately calculated as equivalent to a virtual increase in the area exposed to viscous forces. The general solution obtained is somewhat complicated,[78] but when $h \sqrt{\dfrac{\rho}{\eta T}}$ is a small number, i.e. when the distance h of the fixed from the moving plate is a small fraction of the wave-length of the disturbance produced, the integral may be developed in a series which rapidly converges. For a single disk oscillating midway between two larger disks fixed at a distance $2h$ from each other, Maxwell's formula may be written

$$\delta - \kappa = \frac{1}{2}\frac{\pi a^4 \eta T}{Ih}\left(1 + \frac{4x}{a}\right)\left\{1 - \frac{2}{3}f\delta + \frac{1}{360}f^2(4\pi^2 - 3\delta^2) + \ldots\right\},$$
(IX. 16)

where κ is the portion of the observed logarithmic decrement δ due to the internal friction of the suspension, &c., and $f = h^2\rho/\eta T$. The factor $\left(1 + 4\dfrac{x}{a}\right)$ applies the edge correction, where (cf. § A 2 of this chapter) $x = 2\log_e 2 \cdot h/\pi$. In one of Maxwell's experiments on air, in which, as mentioned in § B 2, three moving disks were used, the value of f amounted to $1/7$ and it was necessary to include two more terms of the expansion involving $f^3\delta$ and f^4.

The use of fixed plates to define the motion of the fluid not only has the advantage of facilitating the mathematical treatment, but also improves the accuracy of the deduction of the viscosity from the experimental data, in that the logarithmic decrement observed is roughly proportional to η instead of to $\sqrt{\eta\rho}$ as in equation (IX. 15). The approximations involved in the calculation are the better justified, and the application of formula (IX. 16) to the reduction of the observations is the more simple, the smaller the value of f.

Maxwell's own apparatus was somewhat massive; the three suspended glass disks, each nearly 1 cm. thick and of 27 cm. diameter, together with their attachments, weighed 3 lb. and were supported by 125 cm. of 0·4 mm. diameter steel wire, which gave them a period of oscillation of 72 seconds. The distance from a fixed to a moving disk varied, in different experiments, from 0·46 to 2·54 cm. In view of the thickness of the oscillating disks the correction x in formula (IX. 16) was increased by $\dfrac{2h'}{\pi}\log_e \sin\dfrac{\pi(h'-\beta)}{2h'}$, where 2β is the thickness, $2h'$ being the dis-

tance between two fixed plates. Using deflexions up to 9°, read on a circular scale of 2 m. radius, Maxwell was unable to detect any variation of the logarithmic decrement with amplitude.   He pointed out that the highest accuracy in the determination of δ should theoretically be obtained by continuing the observations until the amplitude has fallen to $1/e$ of its original value, but the damping was so small in his apparatus that this was not practicable.

Meyer (1871) repeated his earlier experiments after introducing Maxwell's modification of the conditions: later workers, while retaining the bifilar type of suspension preferred by Meyer, simplified the apparatus by using only one moving disk and by reducing its radius so as to facilitate temperature control (Kundt and Warburg 1875, Puluj 1877, Schumann 1882). For relative measurements, in which it is unnecessary to measure the moment of inertia of the suspended disk or its separation from the fixed plates, the dimensions may be still further decreased and a fairly compact apparatus may thus be obtained for the examination of gases and vapours.   Thus Hogg[79] used a thin disk of 4·4 cm. diameter, suspended in a glass envelope by a quartz fibre, and Vogel[80] constructed a similar but slightly smaller viscometer with a platinum wire suspension.   The simplification is carried still further in an all-quartz apparatus described by Braune, Basch and Wentzel[81] which is illustrated in Fig. 42.   The moving disk (diameter 36 mm., thickness 1·5 mm., weight 3·64 gm.) has a short stem at its centre to which a

FIG. 42.   Viscometer of Braune, Basch and Wentzel   (from   *Zeitschrift für physikalische Chemie*).

quartz fibre is fused, 160 mm. long and of such diameter as to give a time of oscillation of 6·5 secs. The fixed disks (diameter 46 mm.) are held 4·5 mm. apart by three pegs fused to their peripheries: they are supported by a stout rod, the upper end of which is sealed through the envelope, the suspension being fused to a small projection from the rod. No mirror is provided, the oscillation being

observed through a window by focusing a micro-telescope on a tiny pointer on the edge of the suspended disk. The fixed and moving disks are ground plane and parallel, and special precautions are taken to mount the oscillating disk midway between and parallel to the fixed plates. An experiment is started by twisting a support which holds the rod protruding from the top of the apparatus, and any vibrations in a vertical plane are allowed to be completely damped before observations are begun. The apparatus has been used, in a cross-shaped furnace, up to 660° C., above which temperature the rapid increase in the hysteresis of the suspension makes the correction for accessory friction large and doubtful. Calibration is effected by determining the logarithmic decrement when the viscometer is filled with dry air at 17° C. The 'natural' decrement κ is found after evacuating to a pressure of less than 1×10^{-4} mm. of mercury.

For a relative viscometer of this type, equation (IX. 16) reduces to

$$\eta = \frac{\delta - \kappa}{TA(1+z)}, \quad \cdot \quad \cdot \quad \cdot \quad \text{(IX. 16 a)}$$

where A is a constant fixed by the dimensions of the apparatus and z is a function of δ and of $h^2\rho/\eta T$. With the small clearances ($h = 1 \cdot 3$ or $1 \cdot 5$ mm.) used by Vogel and by Braune, Basch and Wentzel, the correction z amounts to less than 0·1 per cent. for air, and may be neglected entirely.

5. Oscillation of a cylinder. Meyer[82] considered the problem of a cylinder of radius R and height $2c$ with plane ends, filled with liquid and oscillating about a vertical axis. The equations are similar to those for the oscillation of a disk (§ IV a) but with different signs. He was able to obtain a solution for the case in which $2c$ is small compared with R and e^{-a} is negligible compared with unity, where $a^2 = 2\pi\rho c^2/\eta T$. The solution gives $\sqrt{\eta\rho T}$ as approximately proportional to δ/R^4, but the complete formula involves a tedious succession of numerical and algebraical computations and approximations. The method has not been used except by Mützel,[83] who was able to obtain fairly correct values for the viscosity of some aqueous solutions.

Chella[84] suggested that a compact apparatus suitable for the viscometry of gases at low temperatures might be constructed to observe the oscillations of a cylindrical tube in a cylindrical

annulus full of the fluid. End-effects could be eliminated by comparing the logarithmic decrement with that of a second tube of different material having the same radius and moment of inertia but a different length. Assuming that the oscillating cylinders had internal and external radii R_1 and R_2, moments of inertia I and lengths differing by l, and that the two fixed cylindrical walls had radii $R_1 - c_1$ and $R_2 + c_2$, he found that the difference between the logarithmic decrements δ and δ' of the two cylinders when suspended by the same wire should be related to the viscosity of the medium by the equation

$$\frac{\delta - \delta'}{T} = \frac{\pi \eta l}{I} \left\{ \frac{R_2^3}{c_2} + \frac{R_1^3}{c_1} + \frac{3}{2}(R_2^2 - R_1^2) + \frac{1}{4}(R_2 c_2 + R_1 c_1) + \frac{1}{8}(c_2^2 - c_1^2) \right\}.$$
(IX. 17)

A few determinations were made by Chella with an apparatus constructed on this principle. The suspended cylinders were closed at the top and open at the bottom and the system was small enough to be inserted into a test-tube: to allow for slight differences in the moments of inertia of the two suspended cylinders the formula was modified to

$$\delta - \delta' = \eta \left(\frac{k}{M} T - \frac{k'}{M'} T' \right), \quad . \quad . \quad . \quad \text{(IX. 17 a)}$$

in which form it becomes suitable for relative measurements when the constants k/M and k'/M' have been determined by calibration. It may be noticed that no separate determination is required of the resistance due to friction in the wire, &c., since such effects are eliminated, as are those due to viscous drag on the upper plane end of the cylinder and on the free lower end, by the differential procedure.

Observations on the rate of damping of the oscillations of a solid cylinder suspended in a liquid by a torsion wire were made by Coulomb in 1784 to investigate the adhesion between solids and liquids. A similar apparatus designed to measure the viscosity of oils relative to that of a sugar solution was described by Doolittle[85] and found some application for a few years; but for routine commercial testing it offers no advantages over the usual efflux instruments which are simpler in operation and in calibration.

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MISCELLANEOUS METHODS OF VISCOMETRY

In this chapter we shall deal rather summarily with a number of methods which have been proposed for the measurement of viscosity, but either have received limited application, having been devised for use with a specific type of material, or else give results depending to some extent on surface tension. We shall consider (A) two methods involving flow in tubes, (B) three which depend on the translation of a solid or of a bubble, (C) three in which a constant rate of traverse of a solid surface through the liquid is obtained by externally applied forces, and (D) the twisting of a rod.

(A)

(1) The rate of filling of a capillary tube. This problem has been studied by several investigators, of whom Décharme[1] appears to have been the first. Since drainage effects introduce a complication into the converse problem, that of the rate of emptying of a tube initially full of liquid, considered by Gurney,[2] we shall confine ourselves to the rate of filling of an initially empty tube when one end is dipped into a liquid.

A very detailed treatment has been given by Washburn.[3] For a uniform horizontal capillary, open at both ends and so fine that the driving pressure may be considered to be due entirely to surface tension, he finds that the rate of advance dl/dt of the meniscus is equal to $Cr/2\,l$, where r is the radius of the tube and l the length already occupied. The constant C, which he calls the 'penetrativity' (cf. Rideal[4]) is equal to $\gamma/2\,\eta\,.\,\cos\theta$, where γ is the surface tension and θ the angle of contact. In estimating the viscosity by such a method, γ has to be known or measured with the same accuracy as is desired for η: Washburn suggests, conversely, the use of known viscosities for the estimation of the surface tension.

For the rise of a wetting liquid in an open vertical tube of total length L immersed to a distance h below the level in a jar so wide that it may be regarded as infinite, Washburn's equation 13[3] may be written (cf. Herschel[5])

$$\eta - \eta_A = \frac{r^2 \rho g t}{8} \div \left\{ \left(h + c + \frac{\eta_A L}{\eta - \eta_A} \right) \log_e \frac{b+c}{a+c} - (b-a) \right\}, \quad \text{(X. 1)}$$

where t is the time required for the meniscus to rise from a level b cm. below to one a cm. below that in the jar, η_A is the viscosity

of the air initially in the capillary and $c = 2\gamma/\rho gr$. It is assumed here that $\theta = 0$ and also that the motion is everywhere of the Poiseuille type: for water entering a tube of radius 0·1 mm., the length of tubing in which the latter condition is not satisfied has been calculated by Washburn and by Herschel and found to be negligible unless $(b - a)$ is made very small.

When the capillary rise c is not small compared with h, it is necessary that the wall of the tube be covered with a thin film of the liquid, in order to ensure a zero contact angle; but if the film is of appreciable thickness the time of rise will obviously be shortened. The thickness of the film left when liquid is forced out of an initially full capillary is subject to much uncertainty when the rate of lowering of the meniscus is rapid (cf. Chap. III, § 2 C (3)). The 'Saybolt thermo-viscometer' is a simple instrument designed on the lines above indicated, with $a = 1$ cm., $b = h = 32$ cm., and $r = 0·013$ cm. approximately; it is supplied for commercial tests on kerosene, the depth of immersion being fixed by a mark on the capillary. The liquid is first blown out of the tube by means of a rubber bulb attached to the top; when a stream of air bubbles issues from the lower end, the pressure is released and an observation is made of the time required for the meniscus to rise through the distance $(b - a)$. Herschel[5] made a series of tests on two of these instruments, using liquids having kinematic viscosities from 0·003 to 0·02 cm.²/sec.; he found that the thickness of the film left on the wall by the above method of emptying the capillary caused the times of flow to be approximately 9 per cent. shorter than were indicated by introducing the known values of the dimensions and of viscosity, density, and surface tension into equation (X. 1).

The necessity for an independent estimate of the surface tension might be avoided and the application of equation (X. 1) to the determination of viscosities considerably simplified by the following modification, which would involve little complication of the experimental procedure. Let the level of the liquid in the jar be adjusted, not so as to correspond with a mark on the capillary, but so that the meniscus in the capillary comes to rest at a higher fixed mark. The lengths $(h + c)$ or $(b + c)$ and $(a + c)$ will then become constants of the apparatus which we may call l_1 and l_2: also L may be selected to be so nearly equal to l_1 that the bracketed divisor of equation (X. 1) may be written $\left\{ l_1 \dfrac{\eta}{\eta - \eta_A} \log \dfrac{l_1}{l_2} - (l_1 - l_2) \right\}$,

the surface tension term c being eliminated. A suggestion of this kind was put forward by Fortsch and Wilson.[6] The drainage error found by Herschel might be minimized by substituting for the rubber bulb a pressure system capable of finer regulation, so that the descent of the meniscus before each test may occupy a few minutes instead of a few seconds.

When a liquid of high viscosity is to be examined, a still simpler formula will apply if the rate of entry of the liquid into a capillary under a high driving pressure is observed. If a constant pressure difference P be maintained between the air above the moving meniscus and that above the reservoir and P be so large that the variations of effective pressure due to the hydrostatic head and to the surface tension are negligible, it may easily be shown that the time required for the meniscus to move from a point distant l_0 to a point distant l from the immersed end is given by

$$\eta = \frac{Pr^2t}{4\,(l^2-l_0^2)}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(X. 2)}$$

This is a simplification of the complete equation, involving γ, given by Bosanquet.[7] Measurements of the viscosity of pitch between $65°$ C. and $100°$ C. ($\eta = 5780$ to 120 poises) were made by Pochettino,[9] using capillaries of radius $1 \cdot 1$ mm. or $0 \cdot 8$ mm. into which the pitch was sucked from a test-tube by reducing the pressure in the capillary to 252 mm. of mercury below that of the air.

(2) The oscillation of a liquid in a U-tube.
When a liquid contained in a U-tube of uniform bore is displaced from its equilibrium position by applying to one side a pressure which is then suddenly released, the subsequent motion of the liquid will obviously bear some relation to its viscosity and density. This relation was studied by Menneret[9] experimentally and theoretically. The amplitude of oscillation is corrected for drainage error by the following simple procedure. Suppose the liquid, initially at the level x_0 in one limb (see Fig. 43), is sucked up to x_1 and then allowed to fall: after passing through the equilibrium position to x_2 it rises again to x_3. During this oscillation some liquid is left on the wall and if this had drained completely the last level should have been higher than x_3. By starting the oscillation from a level x_1' below x_0, another value for the second amplitude is obtained, $x_0 x_3'$, which is too high for the same reason. If $x_1 x_0 = x_0 x_1'$, the

true second amplitude is taken as $\frac{1}{2}(x_3 x_3')$. Menneret found that the nature of the oscillation differed according as the damping $(=x_0 x_1/\frac{1}{2} x_3 x_3' = a_1/a_3)$ was large or small.

(i) When $a_1/a_3 > 5$, i.e. $\delta > 1\cdot6$, he found the logarithmic decrement δ constant, i.e. independent of a_1 for a given column of liquid, within the error of observation. Assuming this constancy to be absolute, he regarded the oscillation as being a harmonic one, damped by a viscous force which was proportional to the linear velocity at any moment and calculable by Poiseuille's law. Writing δ for $\log_e(a_1/a_3)$, his equations lead to the results

$$\left.\begin{aligned}\eta &= \tfrac{1}{4}\delta r^2\rho/T \\ T^2 &= 2\pi^2 l/g\,.\,(1+\delta^2/4\pi^2)\end{aligned}\right\} \quad . \quad . \quad . \quad (\text{X. 3})$$

where l is the total length of the column of liquid, measured along the axis of the U-tube, of which the mean radius is r, and T is the time of oscillation. The motion should become aperiodic when $l = \text{or} > \rho^2 g r^4/8\,\eta^2$: Menneret was able to verify this conclusion by gradually varying the length of the liquid column.

FIG. 43. Oscillation of liquid in a U-tube.

(ii) When the damping was slight, he found that the decrement was a parabolic function of the amplitude, i.e. $a_1/a_3 = A_0 + \alpha a_1^2$, where A_0 and α were constants for a given filling of the tube, the value of A_0 being found by extrapolation from a series of observations. The expression for the viscosity became in this case, putting δ_0 for $\log_e A_0$,

$$\left.\begin{aligned}\eta &= \tfrac{1}{4}\delta_0^2 r^2\rho/T \\ T^2 &= 2\pi^2 l/g\,.\,(1+\delta_0^2/4\pi^2).\end{aligned}\right\} \quad . \quad . \quad (\text{X. 3 a})$$

The critical value of a_1/a_3 for the transition from viscous flow, case (i), to turbulent flow, case (ii), would be $a_1/a_3 = e = 2\cdot72$, i.e. $\delta = 1$. The transition was not sharp—rather naturally in view of the differences of velocity during an oscillation—and Menneret found that he could obtain concordant values for viscosity only when a_1/a_3 was greater than 5, i.e. $\delta > 1\cdot6$ (equation X. 3), or A_0 less than $1\cdot85$, i.e. $\delta_0 < 0\cdot61$ (equation X. 3 a). The former case is obviously the more likely to yield accurate results: Menneret

employed tubes with radii about 0·25 cm., $l = 40$ to 70 cm., for experiments in which $\eta = 5$ cp. and one of radius 0·1 cm., $l = 70$ cm. for $\eta = 0·6$ cp., and stated that his values agreed with those of Thorpe and Rodger within 2 per cent.

In a criticism of Menneret's work, Boussinesq[10] stated that his own calculations showed that in the right-hand side of the equation for η (X. 3 a) the coefficient $\frac{1}{4}$ should be replaced by $1/\pi$. The right-hand side of the first equation (X. 3) should, he suggested, be multiplied by $2/\sqrt{3} = 1·155$ to take account of the fact that the velocity distribution is not exactly parabolic (cf. Chap. II, § 4); but the distribution postulated in Boussinesq's amendment cannot hold either near to the menisci or during the reversal of the direction of motion.

Subrahmaniam,[11] apparently in ignorance of any earlier investigation, deduces a solution by a rather different method. Considering only the small oscillations of a column of liquid near the axis, he assumes that the curves representing successive positions of the meniscus of this column will meet on an imaginary circle of radius b; alternatively b is the radius of a fictitious tube, the central column of which has an oscillatory motion identical with that of the central column of the experimental tube, and the velocity distribution across this fictitious tube is parabolic, with no slip at the wall. He assumes further that b is a constant for a given tube containing any wetting liquid. His analysis gives $\eta = \frac{1}{2} \delta b^2 \rho / T$, but the derivation of the coefficient $\frac{1}{2}$ in place of Menneret's value $\frac{1}{4}$ in equation (X. 3) is not obvious. In his experiments he used tubes, of length 84–131 cm., smoothly bent into a U of which the vertical arms were 14–21 cm. apart and found the logarithmic decrements, for liquids having kinematic viscosities 0·0036 to 0·013 cm.²/sec., to be in the same ratio in each of four tubes having radii 0·19 to 0·47 cm.: the maximum discrepancy was about 3·5 per cent. On comparing the results (for water) with his theoretical formula, b was calculated to be from 0·65 to 0·49 of the measured radius, the fraction decreasing as the bore increased. The relative viscosities found by Subrahmaniam are, however, incorrect; values agreeing better with those determined by other means would have been obtained if he had regarded kinematic viscosities as proportional not to δ but to δ_0^2, as in equation (X. 3 a). His logarithmic decrements were in every case lower than those for which Menneret regarded equation (X. 3) as valid, and

the amplitudes were always less than 0·3 cm., so that his observed δ is probably not very different from that for infinitely small oscillations: Menneret used initial amplitudes up to 16 cm.

(B)

(1) The fall of solid bodies of special shape. Any solid of revolution moving along its axis of symmetry at a low speed v through a viscous liquid may be expected to experience a resistance proportional to ηv and to some function of its shape. Just as for the falling sphere (Chap. VIII), the constant terminal velocity of the body falling under gravity will then be inversely proportional to η, and the actual shape will decide what is the maximum velocity (or minimum viscosity) for which this proportionality holds. In general the equations of motion will not be numerically soluble, but the rates of fall in a coaxial cylinder of larger diameter should be a measure of the fluidity over a certain range. Since the form of the body may be selected to meet certain practical requirements, viscometers of this type have proved to be of considerable value in some industries. Thus the Gardner-Parks mobilometer,[12] consisting essentially of a leaking plunger falling in a cylinder of fixed diameter, has been used in several investigations relating to paints. The Hutchinson viscometer[13] and the Consistomètre E.P.C.[14] have been used for many years, in England and in France respectively, for the testing of road tars: these instruments resemble metal hydrometers with a biconical 'bulb' and a stem bearing two graduation marks, loaded by adjustment of the mass so that they sink at a convenient rate when placed in a standard cylinder full of tar. The number of seconds required for the descent through the distance fixed by the two graduations is recorded as the 'viscosity': in view of the low density of the falling body, the relative values obtained are more dependent on the density of the tar than would be the case with a solid metal sphere, but the range of densities of tars is not very large.

In the above-mentioned instruments the clearance between the falling body and the container is considerable and variations of the diameter of the container produce much smaller changes in the rate of fall than similar absolute variations of the diameter of the sinker. The Lawaczeck viscometer[15] operates on a different principle; it consists of a cylindrical metal bulb which falls in a tube of slightly greater diameter. The liquid displaced from the bottom

to the top of the falling bulb has to pass through the narrow annulus between the bulb and the tube. The resistance to the motion of the bulb is made up of three parts, (1) a 'head resistance' due to the form of the stream-lines at the ends, (2) a pressure gradient corresponding with the flow of liquid through the annular channel at a rate fixed by the area of its cross-section and the rate of fall of the bulb (cf. equation IV. 7), and (3) a viscous drag due to the relative movement of two cylindrical walls (cf. equation X. 7). By using a long bulb and a small clearance the importance of the head resistance may be minimized: the resistances (2) and (3) have been calculated approximately by Lawaczeck[15] and in more detail by Heinze.[16] Lawaczeck's formula is

$$\eta = (\sigma - \rho)\frac{(a-b)^3}{3\,b}\frac{t}{s}, \quad . \quad . \quad . \quad . \quad \text{(X. 4)}$$

where σ and ρ are the weights of the bulb and of the liquid per unit volume, a and b the radii of the tube and bulb respectively, and t is the time required for the bulb to fall a distance s. Since the essential dimension $(a - b)$ cannot be measured with the desired accuracy, and will normally vary in different parts of the tube, the instrument is calibrated by means of a liquid of known viscosity and a constant k is obtained which takes account also of the head resistance: hence for a given distance of fall $\eta = kt\,(\sigma - \rho)$.

Tests of a Lawaczeck viscometer are mentioned by Erk,[17] who states that the three bulbs supplied for different ranges of viscosity had diameters 10·0, 11·2, and 11·5 mm., and that the values of the constants determined by calibration with a series of liquids of known viscosity were constant to about ± 2 per cent. at room temperature. The bulbs were about one-third the length of the fall-tube and were provided at each end with three small projections, extending to within 10–15 μ of the wall of the tube to ensure a nearly coaxial fall. Erk found some trouble with bubbles of air in the fall-tube and devised a special stoppered cap to facilitate the filling and to trap bubbles, which are otherwise liable to adhere to the bulb when the apparatus is inverted before starting a test.

For experiments on the variation of viscosity with pressure Bridgman[18] employed a similar method, allowing a steel bulb (Fig. 44) to fall in a steel tube of 6 mm. diameter. The bulb was made in two parts, the perforated cap at the top being a 'push fit' in the main body so that various weights of tungsten or gold might be inserted to accelerate the fall. The length of fall was 3 cm.; the

velocity was also controlled by using bulbs having different clearances, ranging from 0·0125 cm. for tests on water to 0·075 cm. for glycerol. Air was removed by evacuation, so that the bulb was filled with the liquid under test and only the compressibility of the thin walls and of the weights, not that of a sealed bulb, had to be taken into account in determining the effect of pressure. The three guides—shown as two in the Figure—at each end served also to make electrical contact with the wall, the beginning and end of the fall period being indicated by the times at which a circuit was broken or completed through the bulb to an insulated stop, placed off the axis so as to decrease the resistance of the lateral contact. Bridgman calculated that the time required for acceleration to a steady velocity was 0·003 sec., and observed that, with the mechanism used for inverting the system, the bulb began to fall 0·05 sec. before the tube was vertical: these corrections were applied to the electrically

FIG. 44. Bridgman's method.
ᴀ = falling body with guides *g*;
B = insulation; C   steel container.

recorded time, which was nearly always more than a second.

(2) **The rolling-sphere viscometer.** Flowers[19] proposed to measure relative viscosities by timing the rate at which a sphere rolled down the inside of a sloping cylindrical tube in which the liquid was contained. The motion in such circumstances is not amenable to mathematical treatment, but he recorded a number of preliminary observations on the effect of different variables. He found that the velocity of roll was proportional to the sine of the angle of slope only at very small slopes (up to $\sin^{-1} 0\cdot07$ for a steel sphere of 0·1586 cm. diameter in water in a tube of 0·2845 cm. diameter at 20° C.) or at fairly high viscosities (up to $\sin^{-1} 0\cdot8$ for a 1 mm. sphere in a 2 mm. tube full of oil having $\eta = 115$ cp.). The velocity of a given sphere decreased as the diameter of the tube was reduced, the rate of decrease becoming very rapid when

the diameter of the sphere was more than $\frac{3}{4}$ of that of the tube. A 1 mm. sphere in a 2 mm. tube was used for a number of tests on liquids of viscosity 3·5 to 1370 cp., at a slope of 30°: the 'constant' K of the instrument given by $\eta v = K(\sigma - \rho)$ where σ is the density of the sphere, varied by 10 per cent. over this range but by only $3\frac{1}{2}$ per cent. over the range 1 to 115 cp., when the time for water was calculated as 1/5 of that observed at a slope of $\sin^{-1} 0·1$. Among the advantages claimed for an instrument of this type are the smallness of the sample required, the simplicity of the variation of the driving force, and the possibility of making measurements under high pressures.

The last of the above recommendations interested Hersey,[20] who preferred, however, to abandon the use of very small tubes owing to the difficulty of ensuring the required uniformity of bore and surface. With larger tubes and spheres the viscosity is not proportional to the roll time and the calibration may be troublesome. From a dimensional analysis Hersey concluded that when the velocity v was steady the motion could be defined, for geometrically similar systems, by the two non-dimensional quantities

$$\frac{\sqrt{Dg\,(\sigma/\rho - 1)}}{v} \qquad \text{and} \qquad \frac{\eta}{\rho\sqrt{D^3 g\,(\sigma/\rho - 1)}},$$

where D is the diameter of the tube (= a constant multiple of that of the sphere): calibration consists in a determination of the form of the function relating these two arguments. From experiments with a $\frac{1}{4}$ inch steel ball in a 1 cm. diameter tube (ratio of diameters 0·63) at a slope of 15° he found that the relation was linear: it may be rewritten

$$\eta = AD^2 g\,(\sigma - \rho)/v - B\sqrt{D^3 \rho g\,(\sigma - \rho)}. \qquad . \qquad . \quad \text{(X. 5)}$$

With $A = 0·00027$ and $B = 0·0009$, this equation held within the error of observation between $\eta = 0·8$ cp. and $\eta = 800$ cp. and should apply to any such system having the same slope and ratio of diameters provided the roughness is also geometrically similar. The second term on the right of (X. 5) appears to express the effects of eddy resistance and rolling friction.

(3) The air-bubble viscometer. The behaviour of air-bubbles in a liquid which is allowed to rest after being stirred or shaken affords an everyday illustration of the large differences in viscosity which may be encountered in transparent liquids. When one

attempts, however, to render this qualitative observation more precise, difficulties appear not only in the production and measurement of suitably small bubbles but also on the theoretical side (Chap. VIII, § 7). It is possible to make a large bubble rise slowly if the liquid is in a tube which has a diameter so small that the bubble nearly fills the lumen: the rate of rise of such a bubble has been made to serve as a basis of comparison of viscosities in several industries, notably in the manufacture of nitrocellulose and of varnishes. The Cochius viscometer was an early practical development, consisting essentially of a burette tube 50 cm. long, which was closed by taps at each end: the lower tap was so constructed that an air-bubble of constant volume could be displaced through it into the vertical burette tube in which the rate of ascent was measured. An illustration is given in Marshall's 'Explosives'.[21] The influences of the diameter of the tube[22] and the length of bubble on the observed rate were studied by Faust,[23] using a very viscous oil. An experimentally convenient elaboration suitable for the examination of lubricating oils ($\eta = 15$ to 90 cp.) was described by Abrams, Kavanagh, and Osmond.[24]

If the bubble has a length greater than the diameter of the tube, the rate of ascent v is independent of the length of the bubble over a wide range of lengths (Faust[23] and Barr[25]): the increase in driving pressure is balanced by the increased viscous drag. There is, however, no simple relation between the velocity and the diameter or between the velocity and the viscosity, since surface tension is operative in determining the shape of the bubble. At low velocities, in narrow tubes, the ends of the bubble are approximately hemispherical: at higher velocities the bubble becomes bullet-nosed and the rear end more flattened, and one or more rings or thickenings of the film occur near the base. From dimensional considerations it appears that, at speeds so low that inertia effects are unimportant, the motion is defined by the two parameters $y = \eta v/r^2\rho g$ and $x = r/a$, where $r =$ radius of the tube, $a^2 =$ 'specific cohesion' $= 2\gamma/\rho g$ and $\gamma =$ surface tension. A curve is reproduced in my paper[25] which was obtained from experiments with water, glycerol, and oils in tubes of diameter varying from 0·48 cm. to 2·4 cm.; this shows that if the liquid is so viscous that the bubble rises slowly in tubes of over 1 cm. diameter, y may be regarded as constant and independent of surface tension. In this range the velocity is inversely proportional to kinematic viscosity and varies

with the square of the radius. When lubricating oils ($\eta < 100$ cp.) are tested in a tube of a diameter (ca. 0·5 cm.) such as to give a suitable rate of rise, the velocity varies 12 to 15 times as rapidly as the diameter and 6 to 7 times as rapidly as the surface tension for small changes in these characteristics of the apparatus or of the oil. Since, however, the surface tensions of mineral lubricating oils do not normally differ much, approximate comparisons of viscosity may be made in a given tube without unduly large error for workshop purposes.

In all the experiments discussed in the last paragraph, the tube in which the rise of the bubble was observed was adjusted to be vertical and it was remarked that the velocity was considerably affected by errors in the adjustment. Gardner and Holdt[26] describe a method in which the tube may be inclined at a moderate angle to the horizontal, so that a slower rate of travel is obtained without unduly reducing the diameter of the tube. The tubes selected, for viscosities 0·5 to 5 poises, were 110 mm. long and had an external diameter of 13·35 ± 0·05 mm.; gauging of the external rather than of the internal diameter was simple and, with a given batch of tubing, sufficiently accurate for their purpose.[27] Their method is purely comparative, a set of tubes (20 for the above range) being filled to a given height with mineral oils blended to give viscosities increasing by about 0·25 poises: the sample is placed in a similar tube, leaving a bubble of the same length, and the motion of the bubbles in the sample and in a standard is observed when the two tubes are held parallel. It is then easy to determine two limits between which the viscosity lies. Since the temperature coefficients of oils of the same viscosity are not very different, it is only necessary to ensure that the comparison is made at a uniform temperature not too far removed from that at which the standard viscosities were determined: in matching varnishes with the standard oils Gardner and Holdt suggest a deviation of ± 2·5° C. from the specified temperature as allowable.

(C)

(1) Motion of a flat plate in its own plane. The conditions imagined in the definition of the coefficient of viscosity may be fulfilled, barring the requirement of infinite extension, by dipping a plate in the median plane of a narrow rectangular vessel and measuring the steady velocity u attained when the plate is pulled

out by a constant force W. Neglecting edge effects and considering displacements so small that the wetted lengths may be regarded as constant, we have obviously

$$W = -2\,ab\,\eta\,u/h, \quad . \quad . \quad . \quad . \quad . \quad \text{(X. 6)}$$

where $2\,h$ is the width of the vessel and a and b are the lengths of the sides of the plate. The approximation will hold the better the smaller h is compared with a and b, but in order to allow a moderate amount of displacement it will usually be desirable to have the depth of the plate greater than its breadth. An estimate of the correction for the vertical edges may be obtained by Maxwell's method,[28] which consists in adding a hypothetical increment $4\log_e 2 \,.\, h/\pi$ to the actual breadth of the plate when calculating its area. Allowance may be made for the finite thickness $2\,\beta$ of the plate by making the increment

$$4\,(\log_e 2)\frac{h}{\pi} + 4\frac{h}{\pi}\log_e \sin\frac{\pi\,(h-\beta)}{2\,h}$$

and writing $(h - \beta)$ for h in equation (X. 6).

The method has been employed in experiments on plastic materials ($\eta' = 10^7$ poises) by Nutting,[29] who used a plate 50 mm. $\times 100$ mm. at 2 mm. from each of the fixed walls, and in a determination of the viscosity of asphalt (10^{11} poises) by Dudeekij,[30] whose apparatus was on a suitably large scale. Weinberg[30] also deduced viscosities of the order of 10^{16} poises* from the rate of shear of a single parallelopiped under a constant stress.

(2) Axial translation of a cylinder. A somewhat simpler arrangement is that in which a cylinder is pulled in the direction of its length through liquid contained in a second cylinder coaxial with it. Edge effects are thus avoided, leaving only end effects to be eliminated or rendered negligible by the design: it is also easier to maintain a constant thickness of the liquid under shear in different parts of the apparatus. Semi-quantitative observations on the viscosity of super-cooled organic compounds ($\eta > 10^4$ poises) were made by Tammann[32] by observing the rate at which a glass rod of 0·5 mm. diameter was withdrawn from a 12·5 mm. deep layer of 'liquid' in a tube of 1·9 mm. diameter by a force

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* Weinberg gives a review of methods applicable to the study of very viscous materials (η up to 10^{20} poises) and refers to an earlier paper[31] for a bibliography of 52 entries.

equal to the weight of 0·1 gm. The method appears to have been first developed by Segel,[33] who made measurements by its means of the viscosity of sealing-wax from room temperature to 120° C.: it was also used by Pochettino[34] for the study of pitch between 9° C. and 50° C. ($\eta = 2 \cdot 3 \times 10^{10}$ to 5×10^4 poises). Equating the viscous force at any radius to the sum of the applied weight W and the weight of the liquid contained within an annulus extending to that radius, we obtain on intregation

$$2 \pi l \eta u = (W - \pi a^2 l \rho g) \log b/a + \tfrac{1}{2} \pi l \rho g (b^2 - a^2), \quad \text{(X. 7)}$$

where l is the common wetted length, supposed constant, and b and a are the radii of the outer and inner cylinders. When the weight of the liquid is negligible compared with the impressed force, equation (X. 7) simplifies to

$$\eta = \frac{W}{2 \pi l u} \log \frac{b}{a}. \quad . \quad . \quad . \quad \text{(X. 7 a)}$$

The constants of Pochettino's apparatus (Fig. 45) were $l = 12$ cm., $b = 2 \cdot 515$ cm., $a = 1 \cdot 910$ cm.; suitable precautions were taken to ensure that the cylinders were concentric when the pitch was cast into the space between them; the weights applied varied from 0·6 to 5 kg. and the resulting slow descent of a pointer M was observed after magnification. At the highest viscosities some delay occurred before the motion appeared uniform.

(3) Thickness of a drainage film. If a flowing liquid has a free surface, the velocity distribution between this surface and the subjacent solid is similar to that which would occur in a tube obtained by covering the channel with another which was a mirror-image of it (Stokes, 1845)—unless the liquid has a 'superficial viscosity', such as is found in soap solutions owing to adsorption at the interface. The rate of flow down an inclined plane is therefore given by an equation similar to (VI. 1) and might be used to determine the viscosity (cf. Hopf[35]). Redwood[36] illustrates some old forms of 'fluidimeter' in which viscosities were compared by the rate of advance of an oil down grooves in a sloping plate.

When a vertical plane wetted surface is allowed to drain, the thickness of the film of liquid which remains after a given time is approximately proportional to the square root of the kinematic viscosity (Chap. III, § 2, C 3), on certain assumptions. Whalley[37] and Drummond[38] made the weight of oil retained on a microscope

slide after drainage the basis of an approximate comparison of viscosities. Following a method indicated by the Research Staff of the General Electric Company[39] for the estimation of the quantity of liquid carried by a wire passing with a uniform vertical velocity through the surface of a liquid, Stott, Turner, and
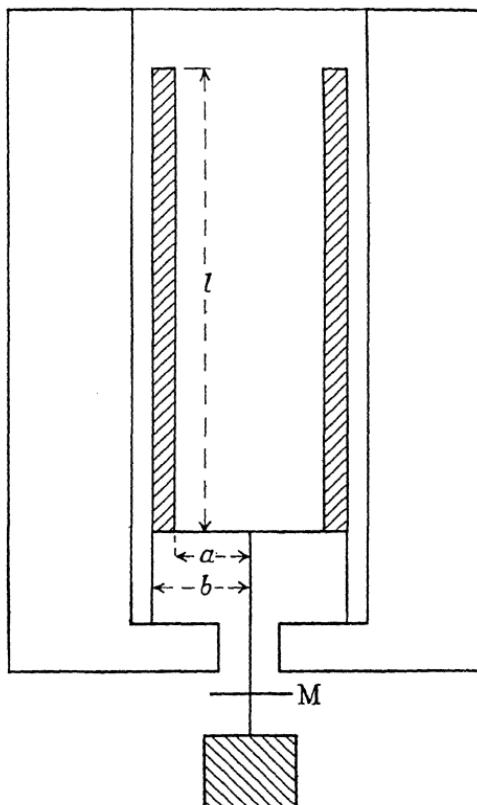
FIG. 45. Pochettino's method for high viscosities.

Sloman[40] have developed a process for the viscometry of glasses between 1000° C. and 1500° C. These authors show that under the conditions of their experiments, in which the velocity v of withdrawal of the wire was 0·015 to 0·9 cm./sec. and the depth of immersion was large compared with the radius a ($= \frac{1}{8}$ mm.) of the wire, the complete dimensional equation reduces to

$$\frac{t'}{a} = f\left(\frac{\eta v}{\gamma},\ \frac{\eta v}{g \rho a^2}\right),$$

where t' is the mean thickness of the glass film withdrawn by the

wire, and γ is the surface tension of the glass. When t'/a and a are so small that the effect of gravity is insignificant, the equation becomes $t'/a = k\eta v/\gamma$. In an appendix to the paper it is explained how a correction may be applied to this equation to take account of the gravitational term by calculating a fictitious surface tension γ' which would give the same film thickness, in the absence of gravity, as is obtained experimentally. The formula is then

$$k\eta = \gamma' t'/av. \qquad . \quad . \quad . \quad . \quad (\text{X. 8})$$

Since the measurements appeared to show that k for glass varied with the rate of shear, i.e. with t'/a, the velocity was always so adjusted that the mean thickness was approximately 1 mm. and a correction for the effect of small variations in thickness was determined; a constant value for k, obtained by indirect calibration, could then be used. For the range of their experiments $k = 2\cdot8$ and γ'/γ was never more than $1\cdot07$, usually about $1\cdot04$.

The method has important advantages in cases where the volume of the liquid under test must be restricted. Stott, Turner, and Sloman heated their glasses in a platin-iridium crucible only 5 cm. high $\times$ 3 cm. diameter at the top. The test consists simply in lowering a wire slowly into the molten glass, raising it at a suitable rate, weighing the deposit and determining the depth of immersion: the glass films contract into beads, so that the observed length of the cold deposit is slightly less than the true depth of immersion. The application of any method of this type is of course practically limited to materials such that the film will set, by cooling or by evaporation, to a solid or much more viscous state soon after being withdrawn from the container. Further, the surface tension needs to be known to the same order of accuracy as is desired in the viscosity measurement. Since the liquid used for calibration has also to fulfil the above requirements, calibration may have to be indirect, via a rotating-cylinder method for example.

(D)

The twisting of a cylindrical rod. A simple method was introduced by Trouton and Andrews[41] for the absolute measurement of viscosities so high (of the order of 10^{10} poises) that rods of the material are only slowly deformed by gravitational flow. When one end of such a cylinder is fixed and a constant torque is applied to

the other end, a constant rate of twisting tends to occur in which the viscous couple due to the shear is equal to the applied couple. Assuming that in the condition of equilibrium two cross-sections, at right angles to the axis and distant dl from one another, have a relative angular velocity $d\omega$, the resultant viscous couple may readily be shown to be $\frac{1}{2}\pi a^4\eta \cdot d\omega/dl$. If $d\omega/dl$ be constant and equal to ω/l over a length l and the torque applied be WR, we have

$$\eta = \frac{2\,WRl}{\pi a^4\omega}. \qquad \cdots \qquad (X.\ 9)$$

Trouton and Andrews prepared rods of pitch ($l = 21$–24 cm., $a = 0.36$ to 0.67 cm.) by rolling between flat boards, and provided the rods with larger tapered square ends for the attachment of the grips. When studying ice, Weinberg[42] froze the cylinder into holes in metal end-pieces, first packing the holes with wet snow. When the rods are not so long that uncertainty as to the effective length of the uniformly sheared portion introduces negligible error, it becomes necessary to measure the rate of twisting by means of gauge marks well clear of the ends, e.g. by attaching mirrors at suitable points. In determining the viscosity of glasses between $450°$ C. and $650°$ C. ($\eta = 10^{14}$ to 10^9 poises), Stott, Irvine, and Turner[43] used long rods of $\frac{1}{2}$ inch diameter, ground for a length of $1\frac{1}{2}$ inches to a diameter of $\frac{1}{4}$ inch, so that the temperature of the part in which most of the twisting occurred might be uniform when the rods were placed in a furnace. On this part of each rod a thin layer of platinum was deposited and three longitudinal lines were engraved; after observing the rate of twisting of the free end, by means of a mirror carried on the shaft to which the torque was applied, the shaft was further rotated while the glass was still hot, to give a total of two revolutions. When the rod was cold the pitch of the helices formed by the engraved lines was measured to find the effective length l: two convolutions of the helix occurred in a length about 8 per cent. greater than the actual length of the narrow portion of the rod, indicating that some part of the flow had taken place in the thicker ends. The form of the helices gave a very sensitive indication of the combined effects of irregularities of diameter and of temperature.

A horizontal cylinder of pitch supported by its ends tends to sag in the middle; indeed Trouton[44] was able to deduce the value of the viscosity from the rate of sagging. Such distortion of the

cylinder is objectionable as complicating the nature of the twist; even if the rod is supported vertically—as in the experiments of Stott, Irvine, and Turner—so that part of its weight is relieved by the lower grip, some gravitational flow may occur tending to cause error in the assumed constancy of diameter. The flow may be avoided, in many cases, by surrounding the rod with a bath of liquid having the same density (cf. Trouton[44]); a vertical arrangement will then usually be preferred. Weinberg[42] has floated a horizontal rod on mercury to avoid sagging, but this device does not prevent the possibility of distortion of the circular cross-section when the viscosity is less than say 10^8 poises.

Trouton and Andrews[41] also used the helicoid torsion method with a tubular specimen (soda glass at $575°$–$710°$ C. with η falling from 10^{13} to $4 \cdot 5 \times 10^{10}$ poises). For a test piece of this form the a^4 of equation (X. 9) has to be replaced by $(a^4 - b^4)$, where b is the internal radius.

In nearly all experiments on very viscous materials in which the rate of shear under a constant force or torque is measured, it has been observed that an appreciable interval must elapse before the rate becomes constant. Thus Trouton and Andrews found that the angular velocity of twist for their pitch rods was initially several times as great as the steady value which was reached after some seconds; and Stott, Irvine, and Turner remark that with a glass of viscosity $10^{16 \cdot 5}$ poises the load must be left on for a number of hours before the definitive readings are taken.

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THE STUDY OF ANOMALOUS SYSTEMS

1. The behaviour of colloidal solutions and suspensions.
Poiseuille's Law was discovered in the course of an investigation
preliminary to an understanding of the circulation of the blood in
the body. It was not until two generations later that the law was
shown to fail when applied to the flow of blood in fine capillaries:
du Pré Denning and Watson[1] suggested a bore of 3 mm. as the
minimum in which proportionality between pressure and rate of
flow could be verified. Garrett[2] had also found that the apparent
viscosities of gelatine, silicic acid, and albumen solutions, as deter-
mined by the oscillating disk method, differed from those found
by a transpiration method and varied with time, &c. In connexion
with the clinical examination of blood Hess, using a capillary
viscometer of his own design, carried out a series of investigations,
published in various medical journals between 1906 and 1915, of
which he gave a summary in 1920.[3] This work, confirmed and
extended by Rothlin,[4] indicated that the 'viscosity' of a given
sample of blood relative to that of water might vary from 6·8 to
7·6 when the driving pressure was altered in the ratio of 6 : 1 ; many
colloidal solutions showed similar behaviour to an exaggerated
extent, in particular those which were capable of setting to gels on
standing or could gelate when used at lower temperatures or in
higher concentrations. The phenomenon appears to be related to
another peculiarity of colloidal solutions, viz. the variation of the
resistance to flow with the time of standing and with the thermal
and mechanical history of the sample. A striking example of this
behaviour is given by Rothlin[4] for a 2 per cent. gelatine solution
at 15·5° C.: when examined $\frac{1}{4}$ hour after its preparation this sol
showed a 'relative viscosity' (compared with water in Hess's
apparatus) varying only from 1·94 to 1·74 as the driving pressure
was increased from 1·25 cm. to 61·85 cm. of mercury: five hours
later the ratios were 8·3 and 3·4 for the same two pressures. This
solution was of course strong enough to set at room temperature,
but a more dilute sol shows a qualitatively similar time effect.

Phenomena of the type here considered have also been studied
by Hatschek. Having indicated, on theoretical grounds, the
probability that the apparent viscosity of an emulsion should vary

according to the rate of shear[5] in certain circumstances, Hatschek made experiments with a rotating cylinder apparatus (Chap. IX, A § III c) and was able to verify his conclusions in the case of a gelatine sol.[6] Later (1916 and 1926), using the same type of instrument, he and his pupils showed that the behaviour of a suspension of starch in an indifferent organic liquid was similar, the 'viscosity' again increasing as the rate of rotation of the outer cylinder decreased. Freundlich and his school (e.g. Freundlich and Schalek[7]) have also examined many colloids in the Hatschek apparatus, and concluded that some sort of rigidity was usually present.

2. Bingham's Law of plastic flow.

To Bingham[8] and Bingham and Green[9] is due the first suggestion of a means for obtaining a quantitative expression of the properties upon which depend the variability of apparent viscosity with the conditions of test. These investigators were working, not with a liquid or colloidal solution, but with relatively coarse and concentrated suspensions, viz. clay slips and well-ground paints. When they plotted the rate of flow of paint through a capillary against the driving pressure, they obtained a straight line which, when extrapolated to zero rate of flow, intersected the pressure axis on the positive side of the origin. Actually, the points representing the lowest velocities observed lay very definitely off the straight line, indicating that the curve might really pass through the origin, but the divergence was tentatively ascribed to a change of régime, viz. to seepage or separation of phases. Neglecting these points, the slope of the straight line was interpreted as representing the 'mobility' (μ)* analogous to the fluidity $(\phi = 1/\eta)$ of a normal liquid, and the intercept on the pressure axis as representing a 'yield value', or pressure below which no flow would occur if there were no change of régime. Bingham's formulation of the 'law of plastic flow' becomes

$$F - f = \frac{1}{\mu} \cdot \frac{dv}{dx}, \quad \cdots \quad \cdots \quad (XI. 1)$$

which is analogous to the law of viscous flow $F = \eta \cdot dv/dx = 1/\phi \cdot dv/dx$; in these equations F is the shearing force per unit area which is required to maintain a velocity gradient dv/dx and f is the yield value which must be exceeded in a plastic material before any flow occurs.

* An unfortunate choice of symbol in view of the wide use of μ, by engineers and hydraulicians, for our η.

In the laminar flow of a liquid through a tube, the velocity gradient, obtained by differentiating equation (II. 2 a), is zero at $r = 0$. On Bingham's hypothesis, the flow of a plastic material through a tube must involve the presence of a central plug, between the particles of which there is no relative movement, carried along by the outer layers which flow according to equation (XI. 1). Integration, with the appropriate boundary conditions, gives for the total rate of discharge

$$Q = \frac{\pi a^4 \mu P}{8 l}\left(1 - \frac{8}{3}\frac{lf}{Pa} + \frac{16}{3}\frac{l^4 f^4}{P^4 a^4}\right), \quad . \quad . \quad \text{(XI. 2)}$$

provided $P > 2 lf/a$ and there is no slip at the wall. If there is a thin layer of expressed liquid, of thickness ϵ and viscosity η between the plastic and the wall, the rate of flow is increased by $\frac{\pi a^3 \epsilon P}{2 \eta l}$. By assuming ϵ/η to be proportional to a, Buckingham,[10] who first carried out the above integration, was able to deduce values of μ, f, and η from Bingham and Green's data for a paint in three tubes, which were practically independent of the dimensions of the tubes. Note, however, that neither (XI. 2) nor the complete Buckingham equation is the equation of a straight line for any value of P above the 'yield', though the experimental points for P much greater than $2 lf/a$ should lie near the asymptote.

Equations similar to (XI. 2) have been obtained by Hencky[11] and by Reiner[12] on the assumption of Bingham's hypothesis. This equation involves an intercept on the pressure axis definitely different from the intercept made by the asymptote. The addition of Buckingham's term for the lubricating film of liquid makes the part of the graph for $P < 2 lf/a$ a straight line passing through the origin. Experimental data for the lowest velocities are usually obtainable only with difficulty and without much accuracy. In recent work on clay suspensions, Scott Blair and Crowther[13] have explored a very wide range of velocities and conclude that Buckingham's equation should be modified, to express their results, by the addition of yet another constant; thus, with our notation

$$Q = \frac{\pi a^4 \mu}{8 l}\left(P - \frac{4}{3}p_2 + \frac{p_2^4}{3 P^3}\right) + \frac{\pi a^3 (P - p_1) \epsilon}{2 \eta l}. \quad \text{(XI. 2 a)}$$

Here p_2 corresponds with Buckingham's $2 lf/a$. Up to a pressure p_1 there is no flow (stage I); next there is a stage (II) in which a rigid plug moves along the tube, with a lubricating film. Above

a certain velocity the surface of the plug is sheared off and a plug moves within a stream-line shell of gradually increasing thickness (stage III): at still higher speeds stream-line flow occurs throughout the tube (stage IV). Using capillaries having bores 0·1 to 0·18 cm., the authors found

I. $p_1 a/l = $ constant for a given clay suspension, provided $l > 110\ a$.

II. In this stage the points lay on a straight line $\dfrac{dQ}{dP} \cdot \dfrac{l}{a^3} = $ constant if $l > 50\ a$.

III. The flow curve in stage III was definitely not a straight line.

IV. At their highest velocities $\dfrac{dQ}{dP} \cdot \dfrac{l}{a^4}$ was a constant; and when the straight line was extrapolated to cut the pressure axis at $c\,(=\dfrac{4}{3}p_2)$, the value of ca/l was constant.

In Fig. 46 I have attempted to illustrate the difference between the formulae of Poiseuille, of Reiner (XI. 2), of Buckingham, and of Scott Blair, exaggerating some of the changes of slope by changing the relative lengths of different parts of the curves (see § 4 with regard to the curve marked Ostwald).

Bingham's hypothesis has been applied by Reiner and Riwlin[14] to calculate an expression for the couple developed in a Couette apparatus by a liquid possessing a 'yield value' or rigidity. The rigidity f is supposed to be such that the inner cylinder moves with the outer until a deflexion is obtained corresponding with a torque $G_0 = 2\pi a^2 hf$, where a is the radius and h the length of the suspended cylinder. Up to this moment there has been no relative motion between the different layers of liquid: thereafter, the thickness of the layer that behaves like a solid decreases with increase in the angular velocity, until the couple indicated becomes $G_1 = 2\pi b^2 hf$, where b is the radius of the outer cylinder. During the mixed régime the relation between torque G and the angular velocity Ω of the outer cylinder is given, after slight rearrangement of Reiner and Riwlin's equation, by

$$G = 4\pi a^2 h\Omega\eta + G_0\,(1 - \log\,G_0/G). \quad . \quad . \quad (XI.\ 3)$$

For couples greater than G_1, when the whole of the liquid is under continuous shear, the expression is

$$G = 4\pi h\,(\Omega\eta + f\,\log\,b/a) \div \left(\frac{1}{a^2} - \frac{1}{b^2}\right), \quad . \quad (XI.\ 3\,a)$$

which may be compared with equation (IX. 9 a). It should be remarked that in a viscometer having the dimensions of Hatschek's the range of torques over which equation (XI. 3) holds would be very limited: for higher speeds the relation between G and Ω would be linear as is evident from (XI. 3 a).
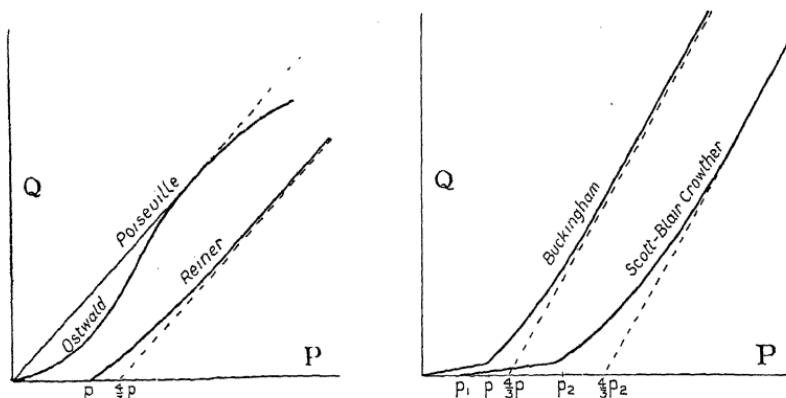
FIG. 46. Flow-pressure diagrams according to various formulae.

3. An empirical relation between pressure and rate of flow.

Although Bingham's method of interpretation of the results of experiments on the 'plasticity' of various clay suspensions, paints, greases, &c., has proved conspicuously successful in many cases, it has not been found possible to fit the approximately linear relation (XI. 2) between Q and P to all the data obtained for colloidal solutions. The most strikingly different behaviour is found among emulsoid or lyophilic sols: nor has a definite yield value of the required order of magnitude been observed in such systems. It has been noticed, however, that when log Q is plotted against log P a straight line is frequently obtained, from which the measured values do not diverge by more than the error of experiment. Such results may therefore be represented by the equation

$$Q = kP^n, \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (XI. 4)$$

the exponent n being greater than unity: Poiseuille's Law would require $n = 1$. Different forms of this relation were proposed first by de Waele[15] from some experiments on petroleum jelly, then by Farrow and Lowe,[16] who used starch pastes, and later by Wo. Ostwald.[17] A recent paper by Ostwald[18] contains references to a number of investigations made in his own and in other

laboratories, demonstrating the inapplicability of equation (XI. 2) and the concordance of the logarithmic relation with data obtained for many different sols.

In experiments with interchangeable capillaries, Farrow and Lowe found the exponent n to be independent of the tube used; the constant k was tentatively equated to $\pi a^4/8 l [\eta]$, the symbol $[\eta]$ being written for the 'coefficient of flow', since they realized that it had not the dimensions of a viscosity. The values obtained for $[\eta]$ varied by as much as ± 10 per cent. in different tubes. Much larger variations of $[\eta]$ with diameter of capillary were found by Herschel and Bulkley[19] for rubber solutions. In more recent work Farrow, Lowe, and Neale[20] have explored a wider range of velocity gradients than was conveniently obtainable in capillary tubes by making measurements also in a rotating cylinder viscometer. The results showed that n increased slowly and $[\eta]$ very considerably, in an extreme case from 28 to 1,400, as the velocity gradient was lowered. They were able, however, to obtain a smooth curve through all the points obtained for any given starch paste by adopting a novel method of plotting, which may be briefly described.

From analogy with equation (XI. 4) the differential equation for the flow of a colloidal solution is written

$$F^n = [\eta] \, dv/dx. \quad \ldots \quad \ldots \quad \text{(XI. 5)}$$

Successive integrations, with the usual boundary conditions (cf. Chap. II, § 3), give for the volume rate of discharge through a capillary tube

$$Q = \frac{\pi}{[\eta]} \left(\frac{P}{2l}\right)^n \frac{a^{n+3}}{n+3} \cdot \quad \ldots \quad \ldots \quad \text{(XI. 5 a)}$$

An equation similar to this, due to Dryden, was first published by Herschel and Bulkley[19] and another form was given by Porter and Rao.[21]

Now the shearing force per unit area *at the wall* is $Pa/2l$. The hypothesis (XI. 5) therefore gives us, after rearrangement of (XI. 5 a) and elimination of $[\eta]$,

$$\left(\frac{dv}{dr}\right)_{r=a} = \frac{Q\,(n+3)}{\pi a^3} \quad \text{(XI. 5 b)}$$

After finding the value for n appropriate to a series of observations of flow through a given capillary under varying pressures, from a

graph of log Q against log P, the Shirley Institute workers then combine the results obtained with different capillaries by plotting (dv/dr) calculated from equation (XI. 5 b) against the shearing stress $Pa/2l$; a logarithmic scale is used to compress the wide range of values into a convenient compass.

Making the assumption (XI. 5) when deriving a relation between the rate of rotation of the outer cylinder and the angle of deflexion of the suspended inner cylinder of a Couette-type apparatus, Farrow, Lowe, and Neale obtain, instead of equation (IX. 9 a),

$$\left(\frac{G}{2\pi a^2 h}\right)^n = 2n\Omega[\eta]\frac{b^{2n}}{b^{2n}-a^{2n}}, \qquad . \quad . \quad \text{(XI. 5 c)}$$

in which $G/2\pi a^2 h$ is the stress at the surface of the suspended cylinder: the linear velocity gradient at the same surface is then

$$2n\Omega b^{2n}/(b^{2n}-a^{2n}), \quad . \quad . \quad . \quad \text{(XI. 5 d)}$$

since by hypothesis $F^n = [\eta]\,dv/dr$. From the rotating-cylinder experiments, n is obtained by plotting log G (or log deflexion) against the logarithm of the time per revolution and then the velocity gradient given by (XI. 5 d) is plotted against the shearing stress, viz. $G/2\pi a^2 h$.

If the hypothesis (XI. 5) were strictly accurate, all the points thus obtained from the capillary tube and the rotation experiments should lie on a straight line, the slope of which would correspond with a constant value of n. Actually the diagram given by Farrow, Lowe, and Neale shows a definite curvature, the value of n increasing towards the lower velocity gradients, especially for the more concentrated pastes. But in view of the facts that the extreme velocity gradients included in the experiments in the two types of apparatus were in the ratio of 1:300,000 and that the points for any given paste all lie on a smooth curve, it is improbable that the method of expression of the results is not an important step towards the discovery of the laws governing the flow of sols.*

In passing, I would suggest that the maximum velocity gradient does not appear to afford the best basis of comparison between the two series of tests. In the rotating cylinder experiments the stress measured is that corresponding with the velocity gradient at the surface of the suspended cylinder, but the volume flowing through

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* For a further development of the method see Rabinowitsch,[22] who obtained similar curves from experiments on nitrocellulose lacquer in which P, l, and a were varied systematically over a wide range.

the capillary tube must be a function not simply of the gradient at the wall but of the average gradient over the cross-section. In purely viscous flow the average velocity gradient is $\frac{1}{3} Pa/l\eta$, i.e. two-thirds of that at the wall (cf. Kroepelin[23]), but on the hypothesis (XI. 5) the average gradient would become

$$\frac{2}{n+2}\left(\frac{Pa}{2l}\right)^n \frac{1}{[\eta]},$$

i.e. $2/(n+2)$ times that adopted above and expressed by (XI. 5 b). The modification suggested does not, unfortunately, tend to straighten the curve found by Farrow, Lowe, and Neale.

A list of twelve empirical flow-pressure equations which have been suggested by various workers is given in a paper by Kraemer and Williamson.[24] Reiner[25] proposes, in addition, a general law of flow obtained by the extension of (XI. 1) into a series developed in powers of $(F-f)$ and containing four physical constants of the material.

4. Elastic modulus and relaxation time. The critical reader cannot have failed to notice a difficulty which arises in attempting to find a physical interpretation of the coefficient $[\eta]$. Not only has $[\eta]$ not the dimensions of a viscosity, but the dimensions depend on the value of n and therefore vary from one system to another. A similar difficulty occurs in the consideration of other phenomena for which empirical laws have been advanced involving varying exponents. In the turbulent flow of fluids in pipes, for example, the resistance has been found to be proportional to a power of the velocity less than the second and varying only slowly over a wide range of velocities. In the case cited, more detailed experiment has shown (Chap. II, § 7) that the resistance per unit area is equal to $\frac{1}{2}\rho v^2 f(vd\rho/\eta)$, so that the occurrence of a varying exponent for v is conditioned by variation of the Reynolds's number, and must be accompanied by a simultaneous change in the exponent of ρ. In the present instance the dimensional difficulty will disappear if we write

$$\left.\begin{array}{l} F = \eta \dfrac{dv}{dr} \cdot f\left(\dfrac{dv}{dr} \cdot T\right) \\[2mm] \eta \dfrac{dv}{dr} = F \cdot f(F/E), \end{array}\right\} \quad . \quad . \quad . \quad \text{(XI. 6)}$$

or

borrowing from Maxwell's *Dynamical Theory of Gases* (1868) the conception of a 'time of relaxation' T and a coefficient of elasticity

E. From an experimental standpoint such a formulation, however, is not more helpful than (XI. 5), since dv/dr cannot be found for a given set of conditions except by assuming a form for the dimensionless function which allows integration of the equation of motion: further, T and E may not be constant. The rate of dissipation of the stress produced by shear has been measured in a few systems (pitch by Trouton and Andrews,[26] a $\frac{1}{2}$ per cent. gelatine sol by Schwedoff,[27] benzo-purpurin sol by Hatschek[28]). The elastic modulus has received more attention, having been determined by Hatschek[28] and by Arcay and Étienne[29] for several sols with apparatus of similar type to that of Schwedoff, by Freundlich and Seifriz[30] using a magnetic method, by Michaud[31] for 0·04 to 0·6 per cent. gelatine sols, and by Bingham and Robertson[32] for an ammonium oleate sol; both Michaud and Bingham measured the axial displacement along a tube which was produced by the application of a known pressure difference, but Bingham studied also the effect of time. The elastic moduli so found have varied from 0·004 to 500 dynes/cm.^{2} According to Maxwell, the viscosity would be equal to ET if the rate of dissipation of stress were proportional to the stress; but the relaxation curves obtained experimentally have always been definitely not logarithmic. In this connexion reference may be made to a recent investigation by Braunbek,[33] who finds qualitative agreement between the results of a study of flow of 'Chatterton compound' and a modification of a theory of plastic flow put forward by Prandtl[34] into which we cannot enter here.

Ostwald[35] adduces evidence to show that the complete velocity-pressure gradient function for the flow of sols through a capillary is S-shaped; the curve is convex towards the pressure axis near the origin and concave at pressures so high as to produce turbulent flow, while between the two portions there may be a straight line corresponding with normal Poiseuille flow. He regards the lower curved portion as indicating a 'structural viscosity', the structure being gradually broken down with increasing rate of shear. In some sols a definite break occurs in this part of the curve which Ostwald ascribes to 'structural turbulence', since it appears at a critical velocity much lower than would be indicated for an apparent viscosity calculated by the usual formulae. Such turbulence has been demonstrated by Hatschek and Jane,[36] and by Andrade and Lewis[37] for an ammonium oleate sol in rotating

straight unless deformed by a larger force. Though the adoption of the force due to gravity as a line of demarcation is arbitrary, the criterion is fairly generally accepted and is moderately sharp; if we call all materials solid which do not flow under a 'very small' force, we shall need to revise our classification every time a more sensitive method of measurement is devised.

Freundlich refers to a 'coefficient of resistance', calculated by the normal equations for any given apparatus. American writers have used the term 'consistency'; Williamson[41] suggests 'pseudo-plasticity' and Scott Blair and Crowther[42] 'pseudo-viscosity' in the 'pachoidal state', but until we know more about the behaviour of sols and elastico-viscous materials it appears rather premature to adopt any formal nomenclature: the phrase 'apparent viscosity' which, though clumsy, has been widely used, does at least proclaim an open mind and is unambiguous. I prefer it to 'viscosity', qualified by quotation marks, for quotation marks are inaudible.

6. Viscometers for the study of anomalous liquids: rotating-cylinder methods. The occurrence of a viscosity varying with the rate of shear may be detected in any of the instruments used for absolute determinations of viscosity in which provision is made for observations under different conditions, e.g. by changing the capillary or varying the pressure applied above the liquid in a capillary-tube viscometer such as that of Bingham (Chap. III, § 1 b), or by varying the rate of rotation, and if necessary changing the suspension wire, in a viscometer of the Couette type. The rate of shear may also be varied, when the viscosity is determined by means of a falling sphere, by using spheres of different diameter or density; the treatment given in Lamb's *Hydrodynamics* (Art. 339) shows that the maximum velocity-gradient (at the equator) is $1 \cdot 5 \, v/a$, i.e. $\frac{1}{3}(\sigma-\rho)ga/\eta$ (cf. equation VIII. 2).

The angular velocity gradient for a normal liquid in the concentric cylinder viscometer is given by equation (IX. 9): eliminating G and η by means of (IX. 9 a), we have for the linear velocity gradient at the surface of the inner cylinder

$$a\left(\frac{d\omega}{dr}\right)_{r\ a} = 2\Omega b^2/(b^2-a^2). \qquad . \qquad . \qquad . \qquad (XI. 7)$$

This is of course merely a special case of equation (XI. 5 d) with $n = 1$. It has frequently been assumed that the rate of shear in a Couette viscometer is constant from one wall to the other: actually

it varies as $1/r^2$, but since the couple is always measured at the inner cylinder, the rate of shear which enters into any comparison of experimental results is not the mean rate but is that above stated. Apparatus of this type appears to be eminently suitable for the detection of the effect of rate of shear on the apparent viscosity of liquids not much more viscous than water, since if a sufficiently fine suspension is used the speed Ω may be reduced to a very low value: it is at the slowest speeds that the anomalies in question are most pronounced. There are, however, many systems, such as the 'thixotropic' sols investigated by Freundlich,[43] in which the structure is so sensitive to mechanical treatment that continued shear in a rotating-cylinder apparatus may prevent or minimize its development. As regards liquids of high viscosity, which may be examined in viscometers with a rotating inner cylinder, we have already referred (Chap. IX, A, § III d) to the possibility of misinterpretation of the influence of pivot friction on the results obtained.

Incidentally, equation (XI. 7) indicates that the rate of shear or linear velocity gradient, which has the same dimensions, $[T]^{-1}$, as Ω, should be expressed in the same units, viz. in radians per second. Hatschek[44] prefers to speak of 'cm. per sec. per cm.', as conveying more directly the idea of a gradient, but the use of such a unit appears liable to provoke incorrect expression of the gradient: thus, if the linear velocity of the outer cylinder is $b\Omega$, and the stationary suspended cylinder is at a distance $(b-a)$, the gradient is not $b\Omega/(b-a)$.

7. Capillary plastometers. Owing partly to the cost of construction of accurate viscometers of the Couette type and partly to lack of familiarity with their use, physical chemists have usually preferred to look for deviations from Poiseuille's Law in capillary-tube viscometers. For systems which are too viscous to be examined in apparatus similar to Fig. 8 or 17 and particularly for those in which the presence of suspended particles precludes observation of a falling meniscus, Bingham[45] recommends the use of a 'plastometer', consisting of a metal cup with detachable top and bottom, which has a glass capillary soldered into the base. The rate of discharge of the contents of the cup through the capillary, when various pressures are applied above the free surface, is determined by weighing the quantity collected in a given time

in a receiver, which is attached by a water-tight joint so that the whole may be immersed in a bath. Instead of breaking this joint every time the pressure is varied, it is often possible to estimate the rate of flow by timing the formation of a number of drops, the weight of a drop being estimated from measurements at the highest and lowest pressures. The change in hydrostatic head due to the loss of material from the cup during any experiment is deduced from the area of cross-section and the total volume collected. Many modifications in the design of the metal work and of the joints of plastometer cups have been made by other investigators, e.g. by de Waele,[46] by Porter and Gruse,[47] and by Browne and Brouse.[48]

An alternative method of measuring the rate of discharge at any moment, which does not involve disturbance of any joints, consists in observation of the rate of displacement of air from the receiver by the entering liquid. For this purpose a gas-tight connexion is made between the receiver and a 'flow-meter', composed of a capillary tube of suitable bore with a sensitive pressure gauge: the rate of escape of the air through the capillary tube into the open or into a large closed reservoir is indicated by the pressure recorded on the gauge, which may take the form of a sloping tube communicating with a cup of much wider section, as in anemometer practice.

Temporary obstruction of the plastometer capillary is recognized by unsteadiness of the flow-meter reading: further, the total absence of flow at low pressures may be confirmed, when it occurs, by closing the capillary of the flow-meter so that it becomes an extremely sensitive leak detector. The flow-meter is most simply calibrated by using it in tests of a normal liquid of known viscosity. This device was included in the set-up described by Green[49] and has been recently adopted also by Scott Blair and Crowther.[50] The latter workers describe a glass plastometer consisting of two cylindrical bulbs connected by ground joints to a horizontal capillary: to avoid corrections for hydrostatic pressure, which become important when low driving pressures are used, the apparatus was suspended from a pivot so that transference of material from one bulb to the other caused a tilt which maintained the two surfaces at the same level. With this arrangement, as in an ordinary viscometer, it is possible to reverse the direction of flow by manipulating certain cocks.

8. Hess's viscometer. The apparatus used by Hess[51] and by Rothlin[52] is similar to Pribram and Handl's first form (Chap. V, § A, 1) in that the capillary and the wider tubes in which the flow is observed lie along the same horizontal axis: hence the diameter of the wide tubes cannot be greater than that which will ensure the formation of a sharp meniscus. Instead, however, of deducing relative viscosities from observations of pressure and time, a direct comparison is made between the rate of flow of the liquid through one capillary and the rate of flow of water through another lying parallel with it. In the apparatus shown in Fig. 47 the two systems of tubes $R_1 K_1 M_1$ and $R_2 K_2 M_2$ are filled from the right end up to the zero marks with water and with the experimental
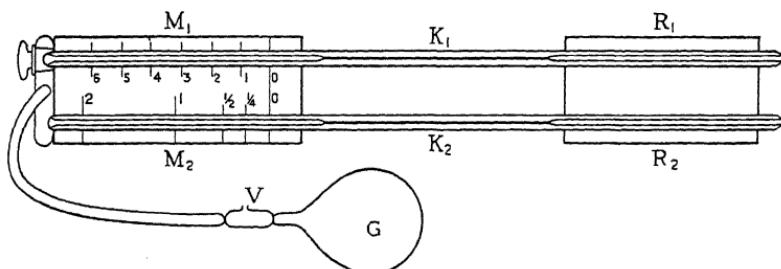
FIG. 47. Hess's viscometer (after the figure in *Kolloid Zeitschrift*).

liquid respectively; then the same suction is applied to both by means of the bulb G. When the liquid reaches the mark 1 in tube M_2 the suction is cut off, and the position of the water meniscus in tube M_1 is read. If the two systems are exactly similar, it is obvious that the relative viscosities of the two liquids are inversely as the volumes, or lengths, which have flowed through the two capillaries in the same time. Allowance may readily be made for differences in bore by finding a factor from a test made with water in both capillaries.

The range of viscosities which can be measured with a given pair of tubes is increased by stopping the flow when the liquid in M_2 reaches other marks such as $\frac{1}{2}$ or 2; if the liquid has a viscosity more than four times that of water, the capillary K_2 would be selected of larger bore than K_1 and calibrated by a water test. The two parallel tubes are mounted in a water-jacket, surrounded by an air-jacket: a bubble of air remaining in the water-jacket serves both to indicate when the system is horizontal and to stir the water.

In the clinical use of the instrument no pressure gauge is necessary; but for tests at different rates of shear an air reservoir and a gauge are included so that the pressure may be fairly constant and known. With high driving pressures the time of flow may be very short, being practically limited only by the rate at which a tap can be turned to make and break the connexion between the capillaries and the reservoirs; if the time is required, e.g. for the application of a kinetic-energy correction, it may be estimated from the pressure readings in a rapid and in a timed slow test. Since there is no change in hydrostatic pressure during an experiment, very low driving pressures may be employed: this circumstance, together with the fineness of the bore, leads to the possibility of exploring very low rates of shear. Surface-tension effects are negligible, since the tubes R and M are of the same bore; but slight errors may arise from the formation of an imperfect meniscus by the advancing column of liquid.

9. The burette consistometer. Of the methods available for obtaining a series of readings of the rate of flow through a capillary under various heads, this, which is due to Cooke,[53] is not only the most rapid, but requires the simplest apparatus. Essentially the consistometer is merely a graduated burette tube with a capillary sealed on in place of the tap: this was the form used by Cooke and by Herschel and Bulkley,[54] and adapted for factory use—by omission of most of the graduations—by Harrison.[55] The flow is started by removing a temporary closure from the orifice, and the times required for the falling meniscus to pass successive graduations of the burette are observed; hence the rates of discharge corresponding with successively smaller heads, measured from the liquid level to the bottom of the capillary, may be calculated. To this straightforward design there are two objections, which, for some purposes, may outweigh the advantages of ease of construction and of cleaning: (i) There is a surface-tension effect at the outlet, where the liquid issues either in drops or as a jet; Herschel and Bulkley showed that a correction calculated by the formula $h'' = 2\gamma/\rho gd'$, where d' is the external diameter of the capillary, gave a close approximation to the 'back pressure' h'' which requires to be subtracted from the measured head, in the case of liquids which wet the glass. (ii) The minimum head available is greater than the length of the capillary: this limitation imposes

restrictions on the length of the capillary or on the range of rates of shear which can be employed with a burette of given length.

Both of these disadvantages are avoided in Auerbach's arrangement,[56] in which the capillary is continued by a U-tube so that the
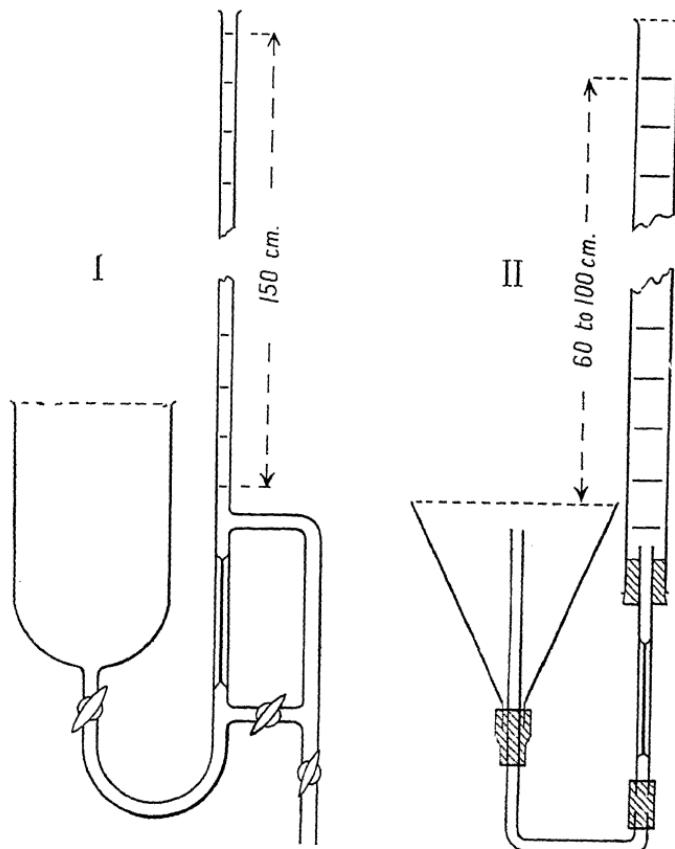
FIG. 48. Burette consistometers (after figures in *Kolloid Zeitschrift*). I. Auerbach's bell-viscometer. II. Ostwald and Auerbach's overflow viscometer.

discharge takes place into a very much wider reservoir, where the liquid is approximately level with the lowest graduation mark of the burette. The two stop-cocks and T-pieces shown on the right in Fig. 48 I serve for filling and emptying the apparatus while it is in a water bath. Even when the wide reservoir has a diameter 10 times that of the burette tube, it is necessary to apply to each of the heads, measured from the position of the falling meniscus at any moment to the final equilibrium position, a correction based on the ratio of the diameters: to avoid this, Wo. Ostwald and

Auerbach[57] designed the overflow viscometer, of which a diagram is given in Fig. 48 II.

Ostwald and Auerbach's method of experiment is to take burette readings l_0, l_1, l_2, ... at equal intervals of time such as will allow about 20 readings to be obtained before the burette is empty. The differences $(l_0 - l_1)$, $(l_1 - l_2)$, $(l_2 - l_3)$, ... &c., are tabulated and their means taken: the volumes, proportional to $\frac{1}{2}(l_0 - l_2)$, $\frac{1}{2}(l_1 - l_3)$, ..., are then divided into the corresponding mean heads represented by l_1, l_2, ..., the zero graduation of the burette (l_∞) being at the lowest level to which the meniscus can fall. The quotients $2l_1/(l_0 - l_2)$, $2l_2/(l_1 - l_3)$ ... are regarded as proportional to the viscosity, and are plotted against the pressures l_1, l_2, ... In some recent work the abscissae used have been not the pressures but the volumes $\frac{1}{2}(l_0 - l_2)$, $\frac{1}{2}(l_1 - l_3)$, ... which flow in the unit of time; these rates of discharge would be proportional to the rates of shear, in the case of a normal liquid.

The burette or 'Fallrohr' used in Auerbach's method is provided with a millimetre scale, and constancy of cross-section is assumed: in some cases the bore is very much greater than is normally available in graduated burettes. Herschel and Bulkley[54] prefer to adapt an ordinary burette graduated in cm.³, and to time the flow of successive 5 cm.³ volumes, by which means considerably greater accuracy is obtained in the determination of rate of discharge: two stop-watches are required unless a split-second watch is used. In view of the larger linear intervals between the graduations concerned it is no longer sufficiently accurate to take the arithmetic mean of the measured lengths as the average head, especially at the lower readings: the average heads are first calculated by the Koch or Meissner formula (III. 9 or 9 a). The use of the Dryden equation (III. 10) will normally be unnecessary since the dimensions will be so selected that the kinetic-energy correction is negligible at the lower heads. Herschel lays considerable stress, however, on the necessity for applying a kinetic-energy correction at the initial high rates of flow, ascribing some of the peculiarities of Ostwald and Auerbach's curves to its omission. The calibration of the consistometer involves a determination of the constants C_1 and C_2 of the corrected Poiseuille equation, written in the form

$$\eta/\rho = C_1 h/Q - C_2 Q. \quad . \quad . \quad . \quad \text{(XI. 8)}$$

Herschel and Bulkley obtain the value of m, the coefficient of

the kinetic-energy correction, by the method explained in Chap. II, § 6 c, from the results furnished by flow tests with several liquids of known viscosity; from these tests they then derive also the mean diameter of the capillary and the values of the constants C_1 and C_2. In the case of a normal liquid a knowledge of these constants and of the average head for each interval suffices for a calculation of viscosity from each observation of rate of flow. If the flow follows the logarithmic law (§ 3) and the exponent of the pressure term is found to be n, the average head h_p to be used in plotting the final flow-pressure curve is shown to be given by the relation

$$h_p^n = (1-n)\ (h_1-h_2)/(h_1^{1-n}-h_2^{1-n}), \quad . \quad . \quad \text{(XI. 9)}$$

where h_1 and h_2 are the measured heads at the beginning and end of a timed interval: when n is considerably greater than unity h_p may differ appreciably from the Meissner head. Presumably also the kinetic-energy term to be subtracted from the average head will differ from that calculated with the normal value of m, but this refinement has not been made since most interest usually attaches to the lower rates of flow.

Burette consistometers of the usual form would not allow sufficiently high pressures to be applied for experiments on stiff pastes: in an adaptation described by Giesy and Arzoomanian[58] the burette contains mercury which is allowed to displace the material under test from a reservoir through a horizontal capillary.

10. Bingham and Murray's method. The rate of flow of a liquid from a reservoir under a constant applied pressure into an empty capillary decreases continually as the capillary fills. If the capillary is horizontal and is open to the air at one end, and the excess pressure effective in producing the flow is P, the pressure gradient at any instant is P/l, where l is the distance of the advancing meniscus from the reservoir end. The volume rate of flow is $\pi a^2 dl/dt$, if a is the radius: a plot of dl/dt against P/l will therefore provide a flow-pressure graph, from which the 'mobility' and 'yield value' may be calculated as in § 2 if the results are of the type there indicated. Bingham and Murray,[59] who first developed this method of plastometry, used a capillary 100 cm. long and noted the times at which the meniscus passed marks at successive 10 cm. intervals. After applying corrections for the hydrostatic head in the container and for the effect of surface tension, they plotted the mean rate of flow, e.g. $\pi a^2 (l_1 - l_0)/t$, where t is the

time required for the meniscus to travel from l_0 to l_1, against $\frac{1}{2} Pa/(l_1 - l_0)$. log l_1/l_0, which was taken as the average of the shearing stresses at the wall. It is evident, however, that for a normal liquid the above rate of flow is proportional to $P/\frac{1}{2}(l_0 + l_1)$, since equation (X. 2) may be written

$$\frac{\pi a^2 (l_1 - l_0)}{t} = \frac{\pi a^4 P}{4 \eta (l_0 + l_1)}. \qquad . \qquad . \qquad . \qquad \text{(XI. 10)}$$

Later workers have hence taken as abscissae the values of $\frac{1}{4}\pi a^4 P/(l_0 + l_1)$, &c.

The method has been used, with slight modifications of the experimental arrangements, by Moness and Giesy,[60] by Kelly,[61] and by St. John.[62] If observations are begun as soon as the liquid has penetrated a short distance into the capillary, a fair range of rates of shear may be obtained in one experiment. It is not advisable, even when normal liquids are under examination, to use pressures so low that the surface-tension correction becomes important, since the correction is affected by the rate at which the liquid wets the tube and by the regularity of the meniscus. As the capillary has to be selected so fine that the linear velocity is low enough for observation, the rates of shear available tend to be much lower than those which are obtainable in plastometers of the Bingham and Green type; while this peculiarity of the method may cause certain relations to be obscured, as pointed out by Green in the discussion on Bingham and Murray's paper, it has the merit of extending the flow-pressure curve towards the origin so that abnormalities may be studied which would not be detected in the older instruments.

The calibration of the capillaries used in this method requires to be carried out in a special manner, since the linear velocity corresponding with any length l of the liquid column is inversely proportional both to the area of cross-section at the head of the column and to the 'resistance' $\Sigma(\delta l/a^4)$ of the length l of tubing. The data obtained from observations of the lengths of a mercury index will apparently be best treated by a graphical method. Bingham and Murray avoided the difficulty by making flow tests with castor oil of known viscosity and calculating an appropriate factor for each of the measured intervals of the capillary.

A somewhat larger range of rates of shear might be obtained by using a vertical capillary, so that the effective head producing the

flow decreased as the capillary filled: the final pressure gradient cannot, however, be made too small, in view of possible error from the effects of surface tension. The equation relating dl/dt with the occupied length under these conditions is not so simple as for the case of a horizontal tube (see references in Chap. X, § A 1), but the apparatus would probably be more convenient. A still greater variation of the velocity of penetration could be secured by closing the capillary with a stop-cock at the exit end, the increases in air-pressure above the meniscus being calculated from the volumetric calibration.

11. Other capillary-tube methods. Variation of apparent viscosity with rate of shear may be demonstrated by comparative determinations in ordinary Ostwald viscometers of different dimensions. In an absolute viscometer, such as was used by Farrow, Lowe, and Neale (see § 3), the rate of shear at the wall, calculated for a normal liquid, is $4Q/\pi a^3$ (cf. equation XI. 5 b). In a completed Ostwald viscometer, though the volume V of the bulb may be readily measured, the radius a will not usually be known with much accuracy. The 'constant' K (equation V. 5 a) will, however, have been determined by calibration with a liquid of known viscosity: the mean rate of shear at the wall may therefore be found by introducing this constant into the expressions $h\rho ga/2l\eta$ or $4V/\pi a^3 t$, whence

$$\left.\frac{dv}{dr}\right)_{r=a} = \frac{hga}{2\,lKt}\,; \qquad a = \left(\frac{8\,VlK}{\pi\,hg}\right)^{1/4}. \quad . \quad \text{(XI. 11)}$$

The mean head h may be obtained with sufficient accuracy by observing the head after half of the total time of flow t: a value for a may sometimes be deduced from the capillary rise when the viscometer contains water. If two Ostwald viscometers have the same water time and the same ratio of l to h, the rates of shear vary as $V^{1/4}$.

Several instruments of the Ostwald type have been described in which different rates of shear are obtained by using different total working volumes, as suggested by Wo. Ostwald.[63] Kruyt[64] filled the wide arm of a long Ostwald viscometer to various heights by means of several pipettes of increasing capacity. Köhler[65] placed filling marks at different levels, above that of the top of the measuring bulb, on a wide arm of uniform diameter, observing the times required for the filling of the measuring bulb, a procedure

which is suitable when opaque or very viscous materials are to be examined. A somewhat similar method was used by Keulegan[66] for extending the viscosity range and assisting the calibration of an instrument of the more usual type in which the time of empty-ing of a bulb is observed, the filling marks in this case being of course lower than the measuring bulb. Slansky and Köhler[67] made the working volumes more exactly reproducible by providing a series of recipient bulbs (Fig. 49) which were filled to marks, $M_1 \ldots M_7$, placed on constrictions above them; with an overall length of some 75 cm. the times of flow for glycerine varied in the ratio 1:15. Herschel[68] describes the construction, manipulation, and calibration of a con-sistometer of the same form, but with a constant working volume and six measuring bulbs.
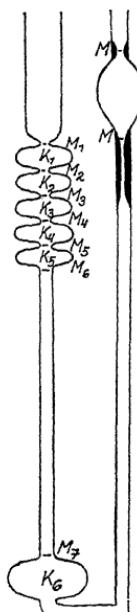
FIG. 49. Viscometer of Slansky and Köhler (from *Kolloid Zeit-schrift*).

A less compact arrangement is that in which additional pressures are applied above the falling meniscus by external means. Wo. Ostwald and Föhre[69] attached above the measuring bulb of an ordinary Ostwald viscometer a connexion to a mano-stat, which consisted simply of a U made of tubing of 3 cm. diameter, with the open arm 200 cm. long, half full of water. Similarly, the American Society for Testing Materials has suggested[70] the application of different air-pressures above the cup of the Saybolt viscosimeter for the characterization of soap-thickened oils, &c. Such methods allow a wide range of velocities to be realized if the viscometer is one which has a low mean hydrostatic head, but the direct evalu-ation of the effective mean pressures for liquids of different density presents difficulties (see Chap. III, § 2 B 3 b). Ostwald and Föhre calibrated their apparatus with glycerin, deducing the relative effective pressures for different settings of the manostat from the relative flow times. The relative mean heads operative with different working volumes in the instruments described in the last paragraph are also estimated from the times of flow observed for a suitable normal liquid.

12. Preparation of 'plastic' liquids for test. Since the ap-parent viscosity of anomalous liquids may vary with their thermal

and mechanical history, it is necessary to adopt some standard treatment before a test is made, if reproducible results are to be obtained. The details will depend on the particular system: a common procedure is to heat the sample to a temperature at which there is no longer any viscometric evidence of 'structure', to cool it under definite conditions and then to maintain it at the temperature at which the flow test is to be made, for a length of time sufficient to develop a uniform consistency. Unless tests are to be made on a 'worked' material it is obviously desirable that the cooling and ageing be carried out in the viscometer. It has frequently been found that after forcing the substance through a capillary a different apparent viscosity is manifested on repeating the test. Farrow and Lowe[71] and Scott Blair and Crowther[72] noted that this effect was absent in the systems, starch paste at 90° C. and clay suspensions, examined by them. If the apparent viscosity is affected by working, those types of apparatus are to be preferred in which results for different rates of shear may be obtained in one continuous operation, as in the burette consistometer.

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OFFICIAL SPECIFICATIONS OF INDUSTRIAL VISCOMETERS

A. THE REDWOOD VISCOMETERS

This specification is taken, by permission, from the Institution of Petroleum Technologists' *Standard Methods of Testing Petroleum and its Products,* 1929.

GENERAL

The Redwood No. I instrument shall be used for all oils the time of flow for 50 ml. of which, at the temperature of the test, does not exceed 2,000 seconds. Oils of greater viscosity are to be tested in a Redwood No. II instrument.

The Redwood Viscometers are unsuitable for use when the time of flow is less than 30 seconds.

It is recommended that viscosity determinations shall be made at one or more of the following temperatures: 70° F., 100° F., 140° F., 200° F., 250° F.

APPARATUS

Redwood No. I Viscometer (Fig. 50)

Oil-cup. The oil-cup is a cylindrical brass vessel, *A*, of 2 to 3 mm. wall thickness, provided with a flange at the base. The upper end of the cup is open and has a plane rim. The bottom of the cup is concave internally to allow complete drainage of the liquid with which it may be filled. It is preferable for ease of cleaning that the internal junction of the bottom of the cup with the sides should be rounded. The flange is provided with a threaded portion by means of which the oil-cup is supported in the water-bath. In order to avoid risk of damage to the jet, it is desirable that the flange be dished so that the projecting end of the jet is above the plane of the bottom of the flange.

The base of the cup is further provided with a tapering central hole into which the jet is fitted and cemented with its bore in the axis of the cup and its bottom surface entirely below the adjacent metal. The level to which the oil is to be filled into the oil-cup is indicated by a stout wire, *B*, soldered into the side of the oil-cup below the oil-level; this wire is turned upwards at right angles and tapered to a sharp point at the precise level for the oil surface. The oil-cup is heavily silver-plated internally to reduce the risk of corrosion.

Internal diameter of oil-cup	.	.	.	46·5±0·5 mm.
Vertical distance from rim to top of bore	.	96·0±1·0 mm.
Height of cylindrical portion of oil-cup	.	86·0±1·0 mm.
Height of filling-point above upper end of bore	82·5±2·0 mm.

Jet. The jet, *J*, is constructed of agate and the central hole is drilled and polished to the greatest possible precision. The upper end of the jet is provided with a concave depression into which fits a ball valve

for starting or stopping the flow of oil. The lower end is convex in order to prevent the outflowing oil from creeping along the base of the oil-cup.

Internal length of jet   .   . 10 ± 0.05 mm.
Minimum internal diameter of jet   1·620 mm.

Water-bath. The cylindrical water-bath, approximately 14 cm. diameter and 9·5 cm. deep and spun from sheet copper, surrounds the
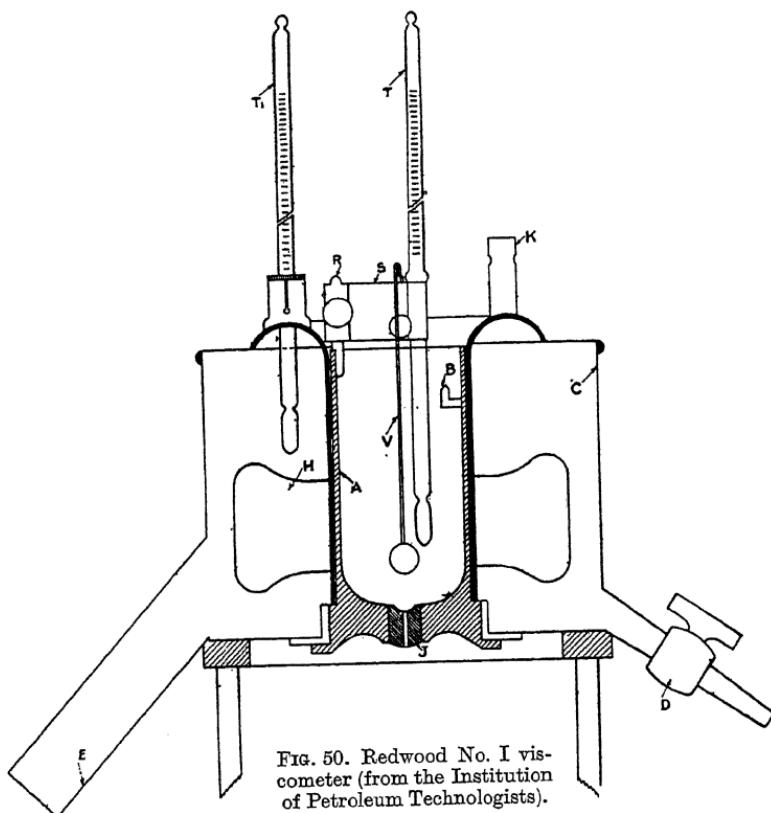
Fig. 50. Redwood No. I vis-
cometer (from the Institution
of Petroleum Technologists).

oil-cup and is provided with a tap for emptying and with a side tube for heating the water or other liquid. The side tube, *E*, about 3 cm. in diameter, is brazed into the bath, the junction being carefully rounded and cleared from projecting metal to allow free circulation of the heated liquid. All joints in the side tube shall be brazed. The copper bath has a stout brass ring brazed into its base; this ring is threaded internally to take the screwed flange of the oil-cup. The joint between the oil-cup and the brass ring is made by a suitable washer.

As an alternative method of heating, the side tube may be electrically heated or may be omitted, and the bath wound externally with suitable resistance-wire for electrical heating, the heating element being applied to the walls but not to the under surface of the bath. Efficient

lagging on the exterior is necessary. Satisfactory electrical heating can also be obtained by mounting an electrical immersion heater within the water-bath in a position as remote as possible from the oil-cup.

Stirrer. The stirring of the bath is effected by means of a cylinder surrounding the oil-cup provided with 4 vanes, *H*, the upper and lower portions of which are turned in opposite directions. A curved shield is fixed to the upper end of the cylinder and extends to within approximately 1·2 cm. of the walls of the bath. This provides both a means of attachment for two insulated handles for rotating the stirrer and a support for the bath thermometer. The cylinder supporting the vanes is cut away between the points of attachment of the vanes to facilitate transference of the heat from the liquid in the bath to the oil-cup. Vertical grooves are also provided on the inner surface of the stirrer cylinder to prevent the liquid in the bath from being carried into the oil-cup when the stirrer is lifted.

Valve. The valve, *V*, for the starting and stopping of the flow of the liquid from the oil-cup consists of a metal ball, approximately 11 mm. diameter, carried on a stiff wire, No. 16 I.W.G. (1·63 mm. diameter), both wire and ball being heavily silver-plated. The upper end of the wire is bent to provide a hook by means of which the valve may be hung on the side of the oil-cup while the oil is flowing through the jet. The fit of this ball valve in its socket must be such that when the cup is filled with an oil of viscosity 300 to 400 seconds the leakage is not more than 2 drops per minute.

Thermometer Support. A spring clip, *S*, approximately 20 mm. in width, is provided to support the oil-cup thermometer, *T*. This clip is carried on a vertical rod, *R*, fixed to the upper edge of the oil-cup opposite the filling-point.

Oil-cup Cover. The oil-cup is furnished with a brass cover fitted with an insulated handle, suitable holes being provided for the oil-cup thermometer and valve wire.

Stand. An iron tripod-stand of suitable height, with levelling screws, supports the bath firmly.

Screen. Attached to the stand is a suitable screen to prevent undue cooling of the under side of the instrument when it is used for tests above 100° F.

Level. A circular level sensitive to 0°·2 mounted on a brass plate to fit the upper end of the oil-cup is provided.

Thermometers.

    (*a*) Oil-cup thermometer—low range.

    (*b*) Oil-cup thermometer—high range.

    (*c*) Bath thermometer.

The thermometers shall conform to the specification as laid down on p. —*.

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* This requires for (*a*) and (*b*), *inter alia*, stems of 5·5–6·5 mm. diameter graduated, for 100–115 mm. immersion, at every 0·5° F. (*a*) 30°–150° F., (*b*) 130°–250° F.

Flask. The 50 ml. flask required as a receiver for the oil must conform to the National Physical Laboratory Class A Standard.

Certification. Each standard Redwood No. I Viscometer shall be marked with the maker's (or vendor's) name and a serial number. Each instrument shall be submitted to the National Physical Laboratory for the purpose of ascertaining whether its general construction and dimensions comply with the requirements of this specification. It will be subjected also to a flow test in comparison with a Standard Reference Viscometer at the Laboratory, and must agree within $\pm 1\cdot5$ per cent. of the time of flow of the Reference Viscometer when tested with an oil the time of flow of which is between 300 and 400 seconds. Instruments complying with this specification and being of the required accuracy will be certified by the N.P.L. The N.P.L. certificate will also state the error corresponding with a time of flow of about 60 seconds.

Redwood No. II Viscometer (Fig. 51)

The Redwood No. II Viscometer is so constructed that the time of efflux of 50 ml. of oil in the instrument is approximately one-tenth of the time in a No. I Viscometer.

It shall be used for all oils the time of flow for 50 ml. of which in the Redwood No. I Viscometer exceeds 2,000 seconds.

Oil-cup. The dimensions of the oil-cup proper, A, are the same as those for the Redwood No. I Viscometer.

The base of the cup is prolonged as a brass tube, B, approximately 25 mm. in outside diameter, into which the agate jet, C, is cemented with its bore in the axis of the cup and its bottom surface entirely below the adjacent metal of the tube (see Fig. 51). The level to which the oil is filled into the oil-cup is indicated by a stout wire, soldered into the side of the oil-cup below the oil level; this wire is turned upwards at right angles and tapered to a sharp point at the precise level for the oil surface. The oil-cup is heavily silver plated internally to avoid corrosion. A screw connexion is provided, by means of which the tube is firmly attached to the bottom of the water-bath, and a recess, 20 mm. deep and 17·5 mm. diameter, is formed below the agate jet.

The oil-cup is held securely in position, for example, by a brass ring, R, round the bottom of the cup, this ring being carried on three legs, L, set at an angle and fastened by screws to blocks in the bottom of the water-bath.

Jet. The jet is constructed of agate, and the central hole is drilled and polished to the greatest possible precision. The upper end of the jet is provided with a concave depression, into which fits a ball valve for starting or stopping the flow of oil. The lower end is convex in order to prevent the outflowing oil from creeping along the base of the oil-cup:

Internal length of jet	.	.	.	$50\cdot0\pm0\cdot2$ mm.
External diameter of jet .	.	.	.	$10\cdot0$ mm. approx.
Minimum internal diameter of jet	.	.	$3\cdot80$ mm.

Water-bath. The bath for heating the liquid is of copper, 0·05 to 0·06 in. thick (16 or 17 I.W.G.), and measures approximately 20·5 cm. in diameter and 18 cm. in depth. It is provided with a tap for emptying and two side tubes, approximately 3·2 cm. in diameter, for heating the contents. These tubes are brazed to opposite sides of the bath. As an alternative method of heating, the side tubes may be electrically heated
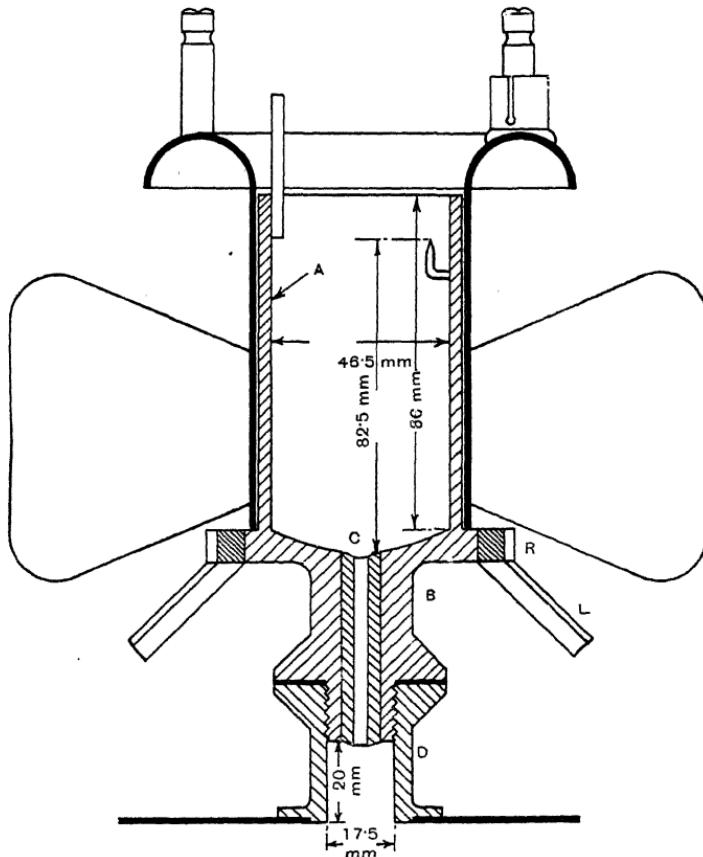
Fig. 51. Redwood No. II viscometer (from the Institution of Petroleum Technologists).

or may be omitted, and the bath wound externally with suitable resistance-wire for electrical heating, the heating element being applied to the walls but not to the under surface of the bath. Efficient lagging on the exterior is necessary. Satisfactory electrical heating can also be obtained by mounting an electrical immersion heater within the water-bath in a position as remote as possible from the oil-cup.

Stirrer. This is similar in construction to the stirrer of the Redwood No. I Viscometer. The curved shield at the top, fitted to avoid splashing of the bath contents into the oil, is of the same diameter as in the No. I

Viscometer—viz. approximately 11·5 cm. outside diameter. The vanes on the stirrer are, however, larger, and have an approximate width of 6·5 cm.

Valve, Oil-cup Cover, Thermometer Support, Stand, Screen, Level, Thermometers, and *Flask* are as laid down for the Redwood No. I Viscometer.

Certification. Each standard Redwood No. II Viscometer shall be marked with the maker's (or vendor's) name and a serial number. Each instrument shall be submitted to the National Physical Laboratory for the purpose of ascertaining whether its general construction and dimensions comply with the requirements of this specification. It will also be subjected to a flow test in comparison with the Standard No. I Reference Viscometer, using an oil the time of flow of which in the No. I Viscometer at the temperature of test is not less than 2,000 seconds. The time of flow in the No. II instrument must not be below 0·096 nor above 0·104 of that obtained in the Standard No. I Reference Visco-meter. Instruments complying with this specification and being of the required accuracy will be certified by the N.P.L.

METHOD

In standard determinations the oil, to eliminate hysteresis, shall be heated in a loosely stoppered container for 1 hour at 212° F. It shall then be cooled to and maintained at 60° F. ($\pm 10°$ F.) for not less than 24 hours before testing.

The oil-cup of the viscometer is cleaned with a suitable solvent (ether, benzene, petroleum spirit, &c.), and then thoroughly dried to remove all trace of the solvent employed. If it is necessary to use any material for rubbing the interior of the oil-cup or for cleaning the jet, such material as will not leave fluff in the oil-cup (e.g. soft tissue paper) shall alone be used. The apparatus is set up and levelled.

The oil, the viscosity of which is to be determined, is heated in a separate vessel to within a few degrees of the temperature at which the test is to be made. The bath of the viscometer is heated to a few degrees above the required test-temperature and the oil poured into the oil-cup through a filter of very fine-meshed gauze. For temperatures up to 200° F. either water or oil may be used in the heating bath; for higher temperatures it is necessary to use oil. The temperature of the bath is adjusted until the temperature of the oil in the cup is maintained at the desired value, the stirrer in the bath being gently rotated at frequent intervals or preferably continuously, and the oil gently stirred during the preliminary period. The oil shall not be stirred during the actual test. When the temperature of the oil has become quite steady at the desired value, the adjustment of the oil-level is made by allowing the oil to flow out until the surface of the oil touches the filling-point. The oil-cup cover is put into position and the test commenced. The clean, dry standard 50 ml. flask is placed centrally below the jet, the neck of the flask being adjusted to within a few millimetres of the

underside of the jet. For tests at temperatures above 70° F. the flask is supported in a beaker packed with cotton-wool or other heat-insulating material to prevent undue cooling during the determination. The valve is then lifted and a stop-watch * simultaneously started. The watch is stopped at the instant the oil reaches the graduation mark of the flask and a final reading of the oil-cup thermometer noted. The test shall be considered invalid if the temperature of the oil varies during the test by more than half a degree for temperatures below 150° F. or by more than 2 degrees for temperatures above 150° F.

<div align="center">EXPRESSION OF RESULTS</div>

Results are expressed as the time in seconds at the temperature of the test. The viscosity in poises (centimetre—gramme—seconds units) can be calculated from the formula:

$$\frac{V}{d} = AT - \frac{B}{T},$$

where:

V = Viscosity of the oil.

d = Density at temperature of test.

T = Time (seconds) for flow of 50 ml.

A and B are instrument constants.

For the standard No. I Viscometer the value of A has been found to be 0·00260 and that of B 1·7, which values will be approximately correct for No. I instruments certified by the N.P.L.

<div align="center">B. THE SAYBOLT VISCOSIMETERS (Fig. 52)</div>

The following specification for the Saybolt instrument is reproduced, by permission, from the 1927 Book of Standards of the American Society for Testing Materials, where it is laid down as the standard method of test for the viscosity of petroleum products and lubricants.

1. (a) Viscosity shall be determined by means of the Saybolt Universal or Saybolt Furol Viscosimeter.

(b) In general the Saybolt Universal Viscosimeter shall be used for lubricants and the Saybolt Furol Viscosimeter for fuel oils and other oils of similar viscosity.

(c) The Saybolt Universal Viscosimeter shall not be used for times of flow less than 32 seconds.

<div align="center">APPARATUS</div>

2. (a) The Saybolt viscosimeters (see Fig. 52) are made entirely of metal. The oil tube, A, is fitted at the top with an overflow cup, B, and the tube is surrounded by a bath. At the bottom of the oil tube is a small outlet tube through which the oil to be tested flows into a

* A reliable stop-watch reading 0·2 second, which is checked at frequent intervals, should be used.

receiving flask, Fig. 52, whose capacity at 20° C. (68° F.) to a mark on its neck is 60 ± 0.15 cc. The outlet tube is of hard and corrosive-resistant metal such as stainless steel, monel metal, &c. The inside diameter of neck of flask, at the level where the graduation mark is placed, is 0·8 to 1·1 cm. The lower end of the outlet tube is enclosed by a larger tube, which, when stoppered by a cork, C, acts as a closed air-chamber and
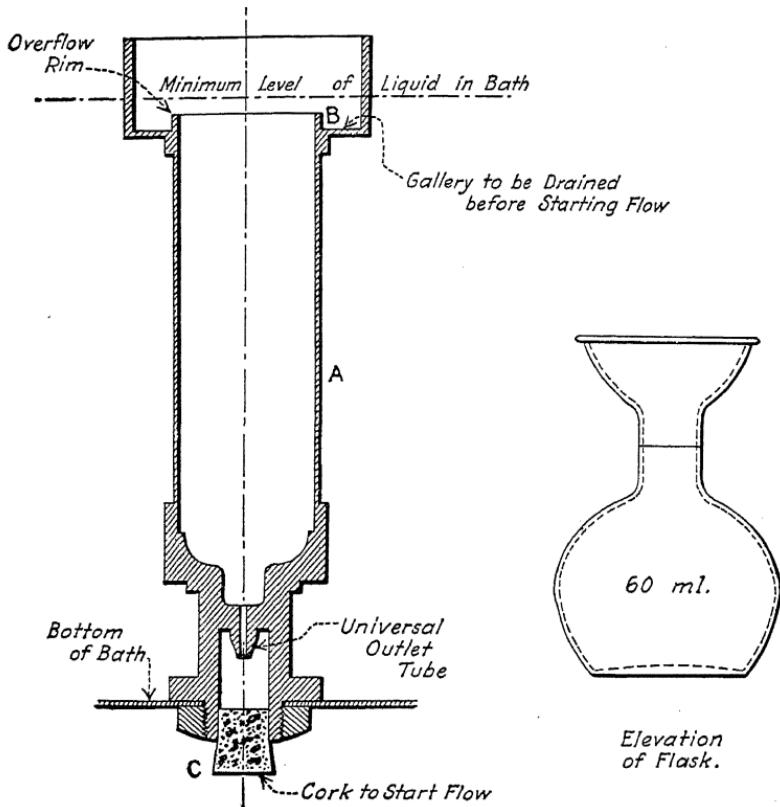
FIG. 52. Saybolt viscosimeter (from the American Society for Testing Materials).

prevents the flow of oil through the outlet tube until the cork is removed and the test started. A looped string may be attached to the lower end of the cork as an aid to its rapid removal. The temperatures in the oil tube and in the bath are shown by thermometers. The bath may be heated by any suitable means. The oil tube shall be thoroughly cleaned, and all oil entering the oil tube shall be strained through a 100-mesh wire strainer. A stop-watch shall be used for taking the time of flow of the oil and a pipette shall be used for draining the overflow cup.

(b) The oil tubes, which may be standardized by the U.S. Bureau of Standards, shall conform to the dimensions given in Table I. The time

of flow shall be within ± 1 per cent. of the time as obtained with the Bureau of Standards' master tube.

(c) The bath and oil tube thermometers shall conform to the following requirements. They cover two sets of 4 thermometers each, one set being graduated in Fahrenheit degrees and the other set in Centigrade degrees, the ranges being chosen to include the temperatures commonly used in testing.

(Here follow detailed technical specifications for thermometers covering ranges of 14° F. (8° C.) in the neighbourhood of 77° F., 100° F., 130° F., 210° F. (25° C., 40° C., 50° C., 100° C.)

TABLE I. *Dimensions of oil tubes.*

Dimensions	Saybolt Universal Viscosimeter.			Saybolt Furol Viscosimeter.		
	Minimum cm.	Normal cm.	Maximum cm.	Minimum cm.	Normal cm.	Maximum cm.
Inside diameter of outlet tube . . .	0·1750	0·1765	0·1780	0·313	0·315	0·317
Outside diameter of outlet tube at lower end . . .	0·28	0·30	0·32	0·40	0·43	0·46
Length of outlet tube* .	1·215	1·225	1·235	1·215	1·225	1·235
Height of overflow rim above bottom of outlet tube * . .	12·40	12·50	12·60	12·40	12·50	12·60
Outside diameter of overflow rim at the top *† . . .	‡	—	3·30	‡	—	3·30
Diameter of container *	2·955	2·975	2·995	2·955	2·975	2·995
Depth of cylindrical part of container .	8·8	—	—	8·8	—	—
Diameter of container between bottom of cylindrical part of container and top of outlet tube * . .	0·9	—	—	0·9	—	—

* This dimension is identical in the Saybolt Universal and the Saybolt Furol instruments.

† The section of overflow rim shall be bounded by straight lines, except that a fillet is permissible at the junction with the bottom of the gallery.

‡ The minimum value shall preferably be not less than 3·2 cm.

TEMPERATURE OF TESTING

3. (a) With the Saybolt Universal viscosimeter, determinations shall be made at 100° F. (37·8° C.), 130° F. (54·4° C.) or 210° F. (98·9° C.).

(b) With the Saybolt Furol viscosimeter, determinations shall be made at 122° F. (50° C.).

(c) Viscosities shall be expressed as . . . . . . seconds, Saybolt Universal (or Saybolt Furol), being the time in seconds for the delivery of 60 cc. of oil.

(*d*) Fuel oils and other oils of similar viscosity showing a time of less than 25 seconds, Saybolt Furol, at 122° F., shall be tested on the Saybolt Universal at 122° F. Oil showing a time of less than 32 seconds, Saybolt Universal, at 122° F., shall be measured in the Saybolt Universal at 100° F. (37·8° C.). These methods of test do not apply to fuels having a viscosity at 100° F. of less than 32 seconds Saybolt Universal, which are not considered to be fuel oils.

<center>PROCEDURE</center>

4. In tests at 100 and 130° F. (37·8 and 54·4° C.) the bath temperature throughout the test shall not vary more than ± 0·1° F. (0·06° C.) from the predetermined temperature which will maintain thermal equilibrium as long as the oil is well stirred with the thermometer. In tests at 210° F. (98·9° C.) a variation of ± 0·2° F. (0·11° C.) is permitted.

Any construction of bath may be employed provided the bath temperature necessary to maintain thermal equilibrium (while the oil in the tube is well stirred by the oil thermometer) is not in excess of 100·25, 122·35, 130·50, and 212·00° F. (37·9, 50·2, 54·7, and 100·00° C.), respectively, for the standard temperatures previously mentioned. The level of the bath liquid shall not be lower than 0·5 cm. above the overflow rim of the oil tube. In tests at 210° F. (98·9° C.) the water-bath shall be vigorously stirred, and may be heated by the direct injection of steam near the bottom of the bath. A bath of other suitable liquid may be used provided it is properly heated and stirred.* The heating and stirring of the bath may be accomplished by any suitable means, provided the source of heat is not less than the following distances from any part of the oil tube: 2 in. (5 cm.) with an external heater, 1¼ in. (3 cm.) with an immersion heater. Viscosity determinations shall be made in a room free from draughts, and from rapid changes in temperature. The room temperature shall be between 68 and 86° F. (20 and 30° C.).†

All oil introduced into the oil tube, either for cleaning or for test, shall first be passed through the strainer.

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* For example, the bath liquid may be water, to which glycerin or salt has been added. In ordinary routine testing it is frequently desirable to employ oil as a bath medium. This is allowable provided the temperature of the oil-bath is adjusted so that the necessary condition of thermal equilibrium is maintained. It is usually necessary to maintain the oil-bath at slightly higher temperatures than are necessary when water is the bath medium. Oil-bath temperatures will need to be from 0·1 to 0·2° F. (0·06 to 0·11° C.) higher for tests at 100° F. (37·8° C.) and 1·5 to 2·0° F. (0·85 to 1·11° C.) higher for tests at 210° F. (98·9° C.) than the corresponding water-bath temperatures.

† These limits are necessary for extreme accuracy in standardization and referee tests, but for routine purposes the use of higher temperatures up to 100° F. (37·8° C.) will not ordinarily cause an error of more than 1 per cent.

To make the test, heat the oil to the necessary temperature and clean out the oil tube. Pour some of the oil to be tested through the cleaned tube. Insert the cork stopper into the lower end of the air chamber at the bottom of the oil tube, sufficiently to prevent the escape of air, but not to touch the small outlet tube.

Heat the oil to be tested, outside the viscosimeter, to slightly but not more than 3° F. (1·7° C.) above the temperature at which the viscosity is to be determined, and pour it into the oil tube until it ceases to overflow into the overflow cup. By means of the oil-tube thermometer, keep the oil in the oil tube well stirred, and also stir well the liquid in the bath. It is extremely important that the temperature of the bath be maintained constant during the entire time consumed in making the test. After the temperature of the bath and of the oil in the oil tube have been constant for one minute at the desired temperatures, withdraw the oil-tube thermometer, quickly remove the surplus oil from the overflow cup by means of a pipette * so that the level of the oil in the overflow cup is below the level of the oil in the oil tube proper; place the 60 cc. flask, Fig. 52, in position so that the stream of oil from the outlet tube will strike the neck of the flask so as to avoid foam. Snap the cork from its position, and at the same instant start the stop-watch. Stir the liquid in the bath during the run and carefully maintain it at the previously determined proper temperature. Stop the watch when the bottom of the meniscus of the oil reaches the mark on the neck of the receiving flask.

The time in seconds for the delivery of 60 cc. of oil is the Saybolt Universal (or Saybolt Furol) viscosity of the oil at the temperature at which the test is made.

With proper attention to details of methods of procedure, duplicate results should not differ from each other by more than 1 per cent.

C. THE ENGLER VISCOMETER (Fig. 53)

The following translation of the specification for the Engler viscometer given in *Zeits. f. angew. Chemie*, 1907, **20**, 833, and in other periodicals of the same date is reproduced by permission of the President of the Physikalisch-Technische Reichsanstalt: the last paragraph of § 2 has been modified in accordance with a notice dated October 1928, issued by the Reichsanstalt (*Chem. Fabrik*, 1928, **1**, 715).

By virtue of an agreement between the Physikalisch-Technische Reichsanstalt of Charlottenburg, the Königlich Preussiche Material-prüfungsamt of Gross-Lichterfelde-West and the Grossherzoglich Badische Prüfungs- und Versuchsanstalt of Karlsruhe, the following specification holds for the testing of Engler viscometers from 1 April 1907.

* It is recommended that the tip of the pipette should be about 2 mm. inside, and about 3 mm. outside diameter, and great care should be exercised to avoid touching the overflow rim while draining the overflow cup.

The testing of the apparatus covers

(1) Dimensions
(2) Determination of the time of efflux with water ('water value').

(1) Dimensions and tolerances (see Fig. 53) :

(a) For the internally gilt vessel G: mm.   mm.
    Width (internal diameter) .   .   .   .   . $106 \pm 1{\cdot}0$
    Height of cylindrical part below the pointers m . $25 \pm 1{\cdot}0$
    Height of the pointers above the lower end of the jet $52 \pm 0{\cdot}5$

(b) For the jet A:
    Length .   .   .   . 20 $\pm\ 0{\cdot}10$
    Internal diameter at the top   .   .   .   . $2{\cdot}90 \pm 0{\cdot}02$
       ,,   ,,   bottom .   .   . $2{\cdot}80 \pm 0{\cdot}02$
    The jet projects below the outer vessel by .   . $3{\cdot}0\ \ \pm 0{\cdot}3$
    Diameter of the projecting part .   .   .   . $4{\cdot}5\ \ \pm 0{\cdot}2$

The jet may either be made entirely of platinum or be coated with a suitably thick layer of platinum. The bore of the jet must be smooth and should not be wavy.

(2) Determination of the time of efflux with water ('Water-value').

The determination of the water-value is performed by finding the time required for 200 cc. of distilled water at 20° C. to flow out of the vessel when it has been filled up to the pointers.

For this purpose the inner vessel and the jet are washed out with ethyl ether or petroleum ether, then several times with alcohol and finally with distilled water.

The viscometer is then set up so that the three points lie in the same horizontal plane. A stopper is next inserted, which is used only for the water test of the apparatus and should never have been in contact with oil. The measuring flask is filled nearly to the brim with distilled water at 20° C., which is poured into the inner vessel: the latter is thus filled to a little above the pointers. The temperature of the water in the inner vessel is maintained at 20° C. by means of the water-bath around it. By raising the stopper a few times, the jet is completely filled with water and the surface of the outlet end is wetted so that a drop completely covering the surface remains pendant. To set the water-level exactly to the pointers, the excess of water is sucked off by means of a small pipette till the pointers are reached. After the apparatus has thus been prepared for the measurement, the stopper is lifted right out and, the surface of the water being absolutely at rest, an observation is made by means of a stop-watch or chronograph of the number of seconds which elapse before the measuring flask is just filled up to the 200 cc. mark. The experiment is repeated several times. The first series of experiments is regarded as finished when three results have been obtained differing by not more than 0·5 seconds and the values show no progressive decrease. The apparatus is then again cleaned and another series of experiments is made. If agreement is obtained with the results

of the first series, no further experiments are required: otherwise they are continued until constant times of efflux are found. The mean of the 6 values of the last two series is taken as the time of efflux of water and is stated on the certificate to the nearest fifth of a second. The time of efflux lies between 50 and 52 seconds for correctly made apparatus.

Accurate determinations must be carried out in a laboratory at about 20° C.
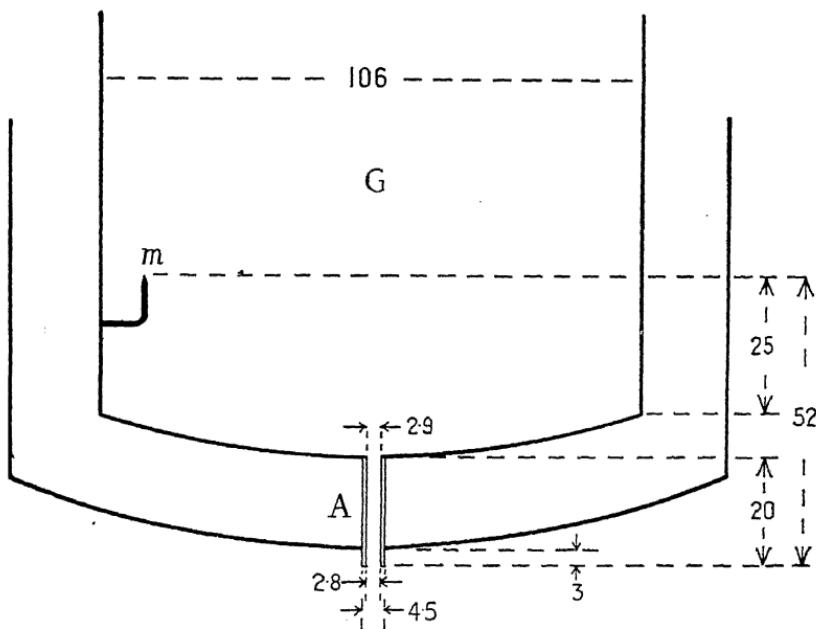
FIG. 53. Engler viscometer.

The thermometers belonging to the apparatus must comply with the regulations of the P.T.R. for liquid thermometers. The measuring flasks used shall be flasks graduated for content (200 cc.) according to § X of the German regulations for calibration. Their total capacity shall be between 250 cc. and 350 cc. They are always to be cleaned and dried before being used for a measurement of the time of efflux with the viscometer.

(3) Certification and Fees.

Viscometers which are found on test to comply with the foregoing specification are stamped on the walls of the outer and inner vessels and on the lid, to show that they have been tested. . . . They are also given a certificate on which appear the results of the tests for dimensions stated in (1) and for time of efflux determined as in (2). . . .

INTERCONVERSION OF VISCOSITY VALUES OBTAINED WITH INDUSTRIAL VISCOMETERS

The subjoined chart, Fig. 54, will be found convenient for converting the indications of various technical viscometers to kinematic viscosities and for intercomparisons. It applies, of course, only to values obtained at the same temperature and assumes that the conversion equations cited are valid at that temperature. The equations used are:

Redwood No. I $\quad \nu = 0.00260T - 1.88/T \quad . \quad (T > 30'')$

Redwood No. II $\quad \nu = 0.0260T - 0.40/T$

Saybolt Universal $\begin{cases} \nu = 0.00226T - 1.95/T & . \quad (32'' < T < 125'') \\ \nu = 0.00220T & . \quad . \quad (T > 200'') \end{cases}$

Saybolt Furol $\begin{cases} \nu = 0.0224T - 1.9/T & . \quad (T < 40'') \\ \nu = 0.0216T & . \quad . \quad (T > 80'') \end{cases}$

Engler $\begin{cases} \nu = E(0.076)^{1 - 1/E^3} \\ \nu = 0.00147T - 3.74/T \end{cases}$

Barbey $\quad \nu = 48.5/(BF).$

On the η/ρ scale the unit is the C.G.S. unit of kinematic viscosity, cm.²/sec. For the Redwood and Saybolt scales (R.I., R.II., S.U., S.F.) the unit is one 'second'; for the Engler instrument two scales are given, one of Engler degrees (E°) and the other of 'seconds' (T_E) uncorrected for water-rate. The scale for the Barbey Ixometer (BF) is in 'Barbey fluidities' (cm.³/hour).

The chart is in three portions, in each of which the readings along the same horizontal line correspond. The scale for $\nu = \eta/\rho$ is uniformly divided and may be used to locate the horizontal position of a thread or transparent index. Thus, joining the graduations $\eta/\rho = 0.15$ in the first portion and $\eta/\rho = 2.5$ in the third, we read in the middle portion the following values corresponding with $\eta/\rho = 0.60$ cm.²/sec.:

Engler degree 7.9, Redwood No. I secs. 235, Saybolt Universal secs. 274, Barbey fluidity 81°, Engler secs. 415, Redwood No. II secs. 23.7, Saybolt Furol secs. 29.6.
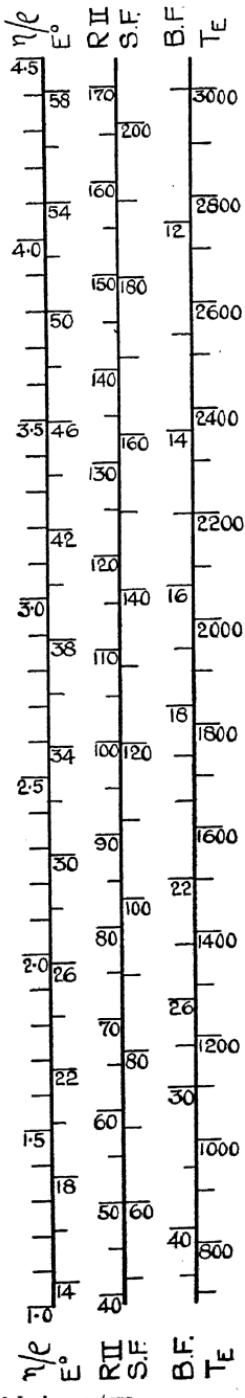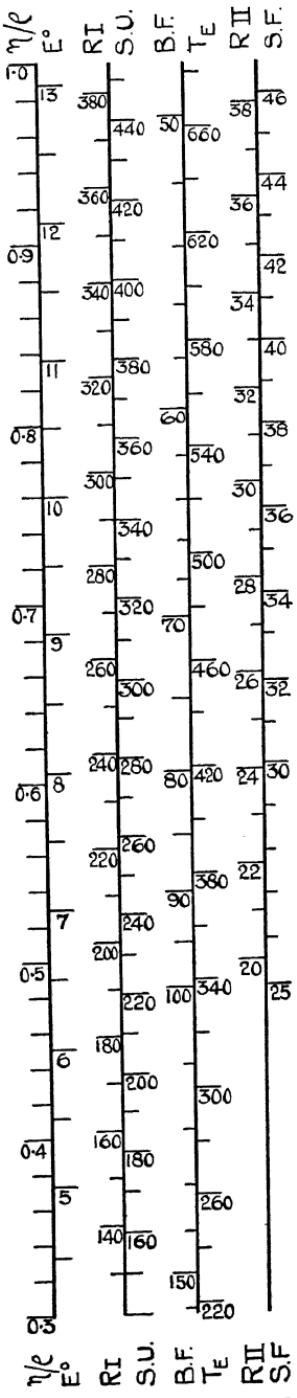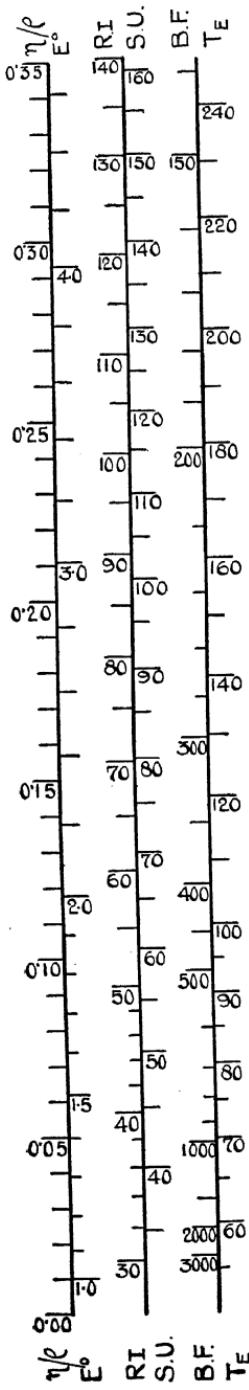
FIG. 54. Chart for conversion of readings of industrial viscometers.

VISCOSITIES OF CALIBRATING LIQUIDS

Water. The table below follows that given by Dorsey in *International Critical Tables*, vol. v, except that the figures in the third decimal place have been rounded off and values for temperatures above 40° C. are given for 5° intervals only. The value at 20° C. is 0·4 per cent. higher than was estimated by Bingham and Jackson (*Bureau of Standards Bull.*, 1917, **14**, 59; *Sci. Paper No. 298*), but is 1 per cent. lower than that given by Leroux (*Ann. Physique*, 1925, **4**, 163). Viscosities are in centipoises.

$t°$ C.	η	$t°$ C.	η	$t°$ C.	η	$t°$ C.	η	$t°$ C.	η
0	1·794	11	1·273	22	0·961	33	0·751	60	0·470
1	1·732	12	1·239	23	0·938	34	0·736	65	0·437
2	1·674	13	1·206	24	0·916	35	0·721	70	0·407
3	1·619	14	1·175	25	0·895	36	0·706	75	0·381
4	1·568	15	1·145	26	0·875	37	0·692	80	0·357
5	1·519	16	1·116	27	0·855	38	0·679	85	0·336
6	1·473	17	1·087	28	0·836	39	0·666	90	0·317
7	1·429	18	1·060	29	0·818	40	0·654	95	0·299
8	1·387	19	1·034	30	0·800	45	0·597	100	0·284
9	1·348	20	1·009	31	0·783	50	0·549		
10	1·310	21	0·984	32	0·767	55	0·507		

Sucrose solutions. Bingham and Jackson (*loc. cit.*) determined the relative viscosities of solutions of purified cane-sugar in water. The table below is abstracted from *International Critical Tables*, where their values were adjusted to suit those for water. (An extended table giving the relation between density and viscosity at 25° C., computed from the original values, is printed in *British Engineering Standards Association Specification No. 188*, 1929). Viscosities in centipoises, concentrations in weights per cent.

$t°$ C.	20 per cent.	40 per cent.	60 per cent.	$t°$ C.	20 per cent.	40 per cent.	60 per cent.
0	3·818	14·82	—	25	1·710	5·206	44·02
5	3·166	11·60	—	30	1·510	4·398	34·01
10	2·662	9·830	113·9	35	1·336	3·776	26·62
15	2·275	7·496	74·9	40	1·197	3·261	21·30
20	1·967	6·223	56·7				

Castor oil. There are no reproducible standard liquids available for viscosities higher than 1 poise. The viscosity of glycerol solutions may vary by 8 per cent. at a given density (Barr, *Aeronautical Research Committee Rep. and Mem. No. 755*, 1921). Refined castor oil was

examined by Kahlbaum and Räber (*Abh. Kaiserl. Leop. Carol. deutsch. Akad. Naturf.*, 1905, **84**, 203), and many investigators have obtained values agreeing closely with theirs; but variations of 2·5 per cent. have been reported. Viscosities found by Kahlbaum and Räber are given below in poises for 5° intervals: the density of their sample was 0·9707 gm./cm.³ at 5° C. and 0·9464 gm./cm.³ at 40° C.

C.	5	10	15	20	25	30	35	40
η	37·60	24·18	15·14	9·86	6·51	4·51	3·16	2·31

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